

PHOSPHORIC ACID, PHOSPHATES, AND PHOSPHATIC FERTILIZERS

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By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company of New York City.

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Chapter I.

Introduction.

Phosphoric acid has always played an essential part in many natural phenomena particularly in the life of animals and plants. With the increase in the manufacture and use of artificial fertilizers it became a highly important commercial factor, and now that new and improved methods are being developed for its more economic production a wider field is opening up for its industrial application—in fact it bids fair to displace sulfuric acid—for a number of purposes, which now require large tonnages of this universally employed reagent.

Nearly all natural and industrial processes are dependent upon carbonic, sulfuric, nitric, hydrochloric and phosphoric acids and the several acids of silica. Either one or more of these relatively simple acids are essential constituents of the vast number of rocks and minerals which constitute the earth's crust. Through their chemical activity the alteration of minerals and the concentration of ore bodies are in part effected. Most of them play a major rôle in the cycle of life and death through the medium of which innumerable organic compounds are built up and again broken down. Finally the arts and industries as practised by man, and through which are evolved the manufactured products so essential to the maintenance and advance of civilization could not be continued unless adequate supplies of these simple inorganic compounds were available.

Sulfuric acid and the acids of silica have so far proven to be the cheapest which are available for industrial use and though they function under widely different conditions (the former being effective at relatively low temperatures and the latter only at high heat) they play more important rôles in manufacturing processes than any of the other acids mentioned above.

The production of all modern structural materials with the exception of limestone and timber) whether they be of steel, copper, cement or glass, is dependent upon the acids of silica. The manufacture of the bulk of our fertilizer materials and the refining and purification of innumerable finished products are brought about by sulfuric acid, in fact all of the other important inorganic acids have been or may be produced through the agency of sulfuric acid.

There is no possibility of any acid being substituted for the acids of silica in most of their industrial applications since silica is either a constituent part of the products sought (products such as cement, glass, tile, brick, etc.) or is present in the raw material (metalliferous ores) as an impurity which can only be removed by taking advantage of its acid properties.

The case of sulfuric acid, however, is quite different, for the chemical activity of this reagent is frequently more important than the product of which it becomes a constituent part, and in many instances after the acid has been partly or wholly neutralized the sulfate radical of the salt or compound formed is relatively valueless or serves only as a carrier of a marketable ingredient. If therefore other mineral acids (such as nitric and phosphoric) which form salts of high commercial value can be produced at a cost materially lower than has been possible by the old methods they might well be substituted for sulfuric acid for a number of industrial purposes and thus the end products obtained be very much enhanced in value.

Recent investigations on the pyrolytic method of producing phosphoric acid and the actual commercial development of this process make it appear that this acid will play a far more important rôle in the industries than it has in the past and that it may actually displace, for certain purposes, large tonnages of sulfuric acid so long considered the most economical reagent which could be employed.

HISTORICAL.

The practice of using phosphatic materials as fertilizers goes back so far that there is no record of when and where they were first employed. The dung of birds was used by the Carthaginians, over 200 years B.C.,¹ and Cato and Columella,² the earliest of agricultural writers, highly recommend the use of pigeon's dung for meadows, corn lands, and gardens. The use of bones, fish, and guano was also a very ancient practice.³ Although the last mentioned material was not introduced into Europe until 1840,⁴ it was used by the Incas of Peru⁵ long before the Spaniards conquered that country and was so highly prized that it was a capital offense to kill the young birds on the guano islands. The effectiveness of dung was attributed by Palissy⁶ in 1550 to the soluble salts contained therein.

¹ Wheeler, H. J. *Manures and Fertilizers*, p. 1.

² Pliny's *Natural History*, Book 17, p. 457; Liebig's *Letters on Modern Agriculture*, p. 239.

³ Fritsch, J. *Manufacture of Chemical Manures*, pp. 39 and 173-175 (1911).

⁴ *Encyclopedia of Agriculture*, Vol. 2, p. 285 (1908).

⁵ *Jour. Roy. Agric. Soc.*, Vol. 2, p. 103.

⁶ Molinari, E. *General & Ind. Chem.*, Vol. 1, p. 643 (1920).

While these three fertilizer materials were for many years the world's chief source of phosphoric acid the nature of this compound was not discovered until long after the isolation and recognition of elemental phosphorus. This element was first prepared in 1669 by Brandt,⁷ an alchemist of Hamburg, Germany, in his search for the philosopher's stone. He evaporated large quantities of urine and obtained a substance luminous in the dark to which he gave the name of phosphorus.

According to Fritsch,⁸ phosphoric acid was discovered in 1743 by Margraff, who ascertained its composition and reconverted it into phosphorus by calcining it with charcoal. No mention is made, however, of the source from which this acid was prepared.

It is stated by several authorities⁹ that Scheele prepared phosphorus by the destructive distillation of bones as early as 1755, but to Gahn,¹⁰ a Swedish chemist, apparently belongs the credit of the discovery that phosphorus is an essential constituent of the bones of men and animals (1769). Ten years later (1779) this same investigator¹¹ found phosphorus in the mineral kingdom as lead phosphate (pyromorphite).

In 1775 Scheele¹² published a description of a method of producing phosphorus, consisting in dissolving bones with nitric acid, precipitating out the lime with sulfuric acid, mixing the concentrated solution with charcoal and heating the mass out of contact with air.

Guano and bones continued to be the main sources of phosphorus and phosphoric acid until after the middle of the nineteenth century, and it is stated that the use of bones was so great in England during the early eighties that the battle fields on the Continent of Europe were turned up to supply Great Britain's demand for phosphates. In 1840 the Duke of Richmond¹³ stated that the fertilizer value of bones was due not to the gelatin and fat but to the phosphoric acid which they contain, and this same year Liebig¹⁴ suggested dissolving bones with sulfuric acid to render the phosphoric acid contained therein more soluble and available to crops. The treatment of bone ash with sulfuric acid is the subject of a British patent issued to John B. Lawes in 1842.¹⁵

⁷ Molinari, E. *General and Industrial Chemistry*, Vol. 1, p. 404 (1920); Thorpe's *Dictionary of Applied Chemistry*, Vol. III, p. 182.

⁸ *Mfr. of Chem. Manures*, p. 1 (1911).

⁹ Molinari, E. *General & Ind. Chem.* p. 404 (1920); Martin, G. *Indust. Chemistry*, Vol. 2, p. 423 (1918).

¹⁰ Thorpe's *Dict. of Applied Chem.*, Vol. 3, p. 182; Watt's *Dict. of Chem.*, Vol. 4, p. 500.

¹¹ Fritsch, J. *Mfr. of Chemical Manures*, p. 1 (1911).

¹² Thorpe's *Dict. of Applied Chem.*, Vol. 3, p. 183.

¹³ Molinari, E. *General & Indust. Chem.*, Vol. 1, p. 645 (1920).

¹⁴ *Des. Engrais Artificiels*, p. 4 (1846); *Organic Chem. in its Application to Agriculture & Physiology*, p. 184-185 (1840).

¹⁵ British Patent 9353 (1842).

This discovery marked the beginning of the immense acid phosphate industry which is the basis of the fertilizer business in this country. In 1845 soon after this epoch making practise was introduced, low grade mineral phosphates known as coprolites were discovered in England,¹⁶ and four to seven years later (1849-1852) medium and low grade deposits of this mineral were recognized in several departments in France.¹⁷ The direct use on the soil of these mineral phosphates in a finely ground condition was advocated by Elie de Beaumont¹⁸ in 1856, but Liebig pointed out in 1857 that such phosphates could be dissolved with sulfuric acid just as readily as bone and thus rendered more efficient for agricultural purposes. So eagerly was this process taken up that five years later (1862) the annual production of superphosphates in England had reached 200,000 tons.

Phosphate baking powders were introduced into the United States at an early date, and a patent issued to E. N. Horsford¹⁹ claims a substitute for tartaric acid in such products. The inventor called this substitute "Pulverulent Phosphoric Acid," but his description of the method by which it was prepared shows it was actually a rather pure dry monocalcium phosphate mixed with either flour or starch.

Until relatively recent years the phosphoric acid in baking powders was derived almost entirely from bones but with improvements in methods of purification and the commercial development of the pyrolytic process of producing this acid, phosphate rock is being used as a raw material in ever increasing quantities.

Since 1867, when phosphate rock was first developed in South Carolina,²⁰ the United States has been the foremost phosphate producing nation in the world, not only supplying its own agricultural demands but a large proportion of the requirements of certain European countries.

In 1877 two Englishmen, Thomas and Gilchrist, developed a process in which phosphatic iron ores which were up to that time considered of relatively little value, could be used in the production of steel low in phosphorus by causing this element to enter a highly basic slag.²¹ The phosphorus in this slag while not in a water soluble form, was found to be readily available to plants and quite effective in increasing

¹⁶ Fritsch, J., *Mfr. of Chem. Manures*, p. 26 (1911).

¹⁷ *Idem.* p. 14.

¹⁸ Molinari, F. *General & Indust. Chem.*, Vol. I, p. 645 (1911).

¹⁹ U. S. Patent No. 14722 (1856).

²⁰ Bull. 18, U. S. Dept. Agric. (1913); *Phosphate Rock in 1921 Mineral Industry* 1922.

²¹ British Patents Nos. 4422 (1877); 289, 908, 2835, 4063 (1878); 1079, 1313, 1711, 2162, 5302 (1879); 388, 4285 (1880); *Jour. Iron and Steel Institute*, p. 120 (1879); *Idem* p. 407 (1881).

crop yields. This discovery placed another large source of phosphoric acid at the disposal of the farmer and several of the more progressive nations of Europe have been depending largely on basic slag to supply their agricultural demands for this fertilizer ingredient.

The effectiveness in the field of such slightly soluble materials as bones and basic slag led to the search for methods of determining the availability of these materials in the laboratory. Certain conventional test solutions have therefore been established which are intended to approximate the solubility effect of the soil waters, and the commercial values of phosphates are to a large extent based upon their complying with these tests. These regulations coupled with the fact that a certain amount of prejudice exists towards fertilizers of an acid nature have encouraged investigators to study other methods of treating phosphate rock besides that of rendering it soluble by the aid of sulfuric acid, but up to the present few have been commercially successful. A number of such typical schemes are discussed further on and complete classified lists of these processes are given in the tables of the Appendix to this monograph.

ELEMENTAL PHOSPHORUS, OXIDES OF PHOSPHORUS AND THE ACIDS OF PHOSPHORUS.

While this treatise deals chiefly with orthophosphoric acid and its compounds, the orthophosphates, certain derivatives of this acid are so closely related thereto and play such important rôles in the laboratory as well as in factory practise that to ignore them would sacrifice clarity and render the discussion of the main subject rather incomplete. It is necessary, therefore, to devote some space to descriptions of the occurrence, properties, and methods of preparing elemental phosphorus and its various other oxides and acids.

Phosphorus.

This element though widely distributed in nature is never found in a free or uncombined state because of its great affinity for oxygen. With one or two minor exceptions²² it exists in the mineral kingdom only in the form of phosphates of which a large number have been identified.

As ordinarily prepared elemental phosphorus is a white or slightly yellow waxlike substance which becomes brownish yellow on exposure to light due to the formation of some red phosphorus. It has a specific gravity of 1.83, a melting point of 44.4° C and a boiling point of 287° C.

²² Phosphorus occurs as iron phosphide in meteorites.

It is insoluble in water but dissolves readily in carbon disulfide (18 to 1) from which it crystallizes in rhombic dodecahedra; it is also very soluble in the halogen compounds of phosphorus, and slightly so in alcohol, ether, benzene, xylene, methyl-iodide, glycerine, acetic acid and fused stearic acid. Phosphorus is luminous in the dark possibly due to the formation of hydrogen phosphide (PH_3) which burns in the air. Other authorities explain phosphorescence on the ground that a preliminary oxidation of P to P_2O_3 takes place and this latter compound is oxidized further with simultaneous production of ozone, the surrounding air becoming ionized. This phenomenon of phosphorescence, however, is regarded by others as very complex. Moist phosphorus oxidizes rapidly in the air, evolving white fumes of phosphorous and phosphoric acids and phosphorus pentoxide. At slightly elevated temperatures or when finely divided, it takes fire spontaneously in the air, burning to phosphorus pentoxide. Molinari,²³ however, states that it does not oxidize and may be distilled in pure dry oxygen.

White or yellow phosphorus is very poisonous, 0.1 gram being sufficient to cause death. Post mortems have shown that the element is absorbed in the liver (which is distended), and in the blood. The chronic disease contracted by those who work in factories where yellow phosphorus is extensively used is known as necrosis of the bones, especially of the teeth and jaw. This disease was formerly quite prevalent among employees of match factories before the use of yellow phosphorus in matches was prohibited by law.

Phosphorus was first prepared in commercial quantities from bones and bone ash. Briefly the method consisted in treating calcined or degelatinized bone with sulfuric acid, filtering or decanting off the solution of phosphoric acid or, monocalcium phosphate from the gypsum, evaporating the solution to a specific gravity of 1.45, mixing it with 20 per cent of charcoal or coke and again heating in shallow pans till the mass contained not over 6 per cent of moisture. This mixture was then placed in terra cotta retorts which in turn were introduced into a suitable furnace and heated to redness for 24 hours, and then to a white heat for 48 hours. The phosphorus distilling off was collected under water and subsequently purified by redistilling.

This method of making phosphorus was cumbersome and costly and gave relatively low yields. It has been largely supplanted by the electric furnace process in which an intimate mixture of the raw phosphate rock, silica and carbon (coke) is introduced into an arc furnace and smelted directly without access of air. Not only does this method render the use of sulfuric acid unnecessary but the process is continuous and the yields obtained are much higher. A modification of this

²³ General and Industrial Chemistry Part 1, p. 403 (1920).

general process is now being successfully employed in the manufacture of phosphoric acid so is discussed in detail further on in this publication.

Two allotropic forms of phosphorus are known; namely, red and black phosphorus, which are denser and have lower specific heats than the white variety. Black phosphorus is obtained by crystallization of the element from solution in molten metal, or by heating red phosphorus for a long period at 360° C. in sealed tubes. It has little or no commercial significance and some authorities doubt the existence of this allotropic form of the element.

Red or so-called amorphous phosphorus, discovered by Schrotter in 1845 and later found to really crystallize in the hexagonal system is formed by exposing yellow phosphorus to light for a long period, or by heating it to 300° C. out of contact with air. This variety is not phosphorescent, does not alter in the air, is nonpoisonous and is not readily set on fire by friction, in fact is not combustible until heated to a temperature of 200° C. Advantage is taken of its nonpoisonous character in the industries and it is now substituted for the yellow variety in a number of commercial operations.

Oxides of Phosphorus.

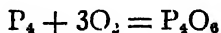
There are four oxides of phosphorus, namely phosphorus suboxide (P_4O), phosphorus oxide (P_4O_6), phosphorus tetroxide (P_2O_4) and phosphoric pentoxide (P_2O_5). Only two of these oxides, however, have much stability or importance commercially.

Phosphorus Suboxide (P_4O).

This compound has only been made as an interesting laboratory experiment. The usual method of preparation consists in dissolving yellow phosphorus in an alcoholic solution of potassium hydroxide. Hydrogen and phosphine are thus evolved and a bright red liquid remains which when acidified deposits a gelatinous mass composed mainly of P_4O . On filtering and repeatedly freezing, this oxide may be obtained in a relatively pure state as an orange colored hygroscopic substance which readily burns to the higher oxides of phosphorus.

Phosphorous Oxide or Phosphorous Anhydride (P_4O_6).

This oxide of phosphorus is obtained when yellow phosphorus is gently heated in a limited amount of dry air.

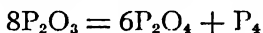


A certain amount of phosphoric anhydride (P_2O_5) is also formed at the same time but the former oxide being more volatile than the latter may be readily separated by sublimation.

Phosphorous oxide possesses a peculiar phosphorus-like odor. It forms white crystals which run together into a waxlike mass melting at $22\frac{1}{2}^{\circ}$ C. It readily sublimates and boils out of contact with air at 173° C. Its vapor density shows its formula to be P_4O_6 and not P_2O_3 as formerly supposed and even now often expressed in writing chemical reactions involving its use. When dissolved in cold water phosphorous oxide forms a mixture of meta-phosphorous acid (HPO_2) and phosphorous acid (H_3PO_3). With hot water it produces red phosphorus and phosphoric acid (H_3PO_4). Phosphorous oxide oxidizes very readily, catching fire in the air and burning to P_2O_5 .

Phosphorus Tetroxide (P_2O_4).

By heating phosphorous oxide to 400° C. phosphorus tetroxide (P_2O_4) and red phosphorus are produced thus.



The tetroxide of phosphorus forms transparent crystals which react with water producing phosphorous and phosphoric acids. This oxide may be regarded as a mixture of phosphorous and phosphoric anhydrides just as nitrogen tetroxide (N_2O_4) is considered a mixture of nitrous and nitric oxides.

Phosphorus Pentoxide or Phosphoric Anhydride (P_2O_5).

This compound is the final product obtained by the complete oxidation of phosphorus. It is by far the most important of the oxides of phosphorus and the most readily produced since all of the lower oxides tend to change over into this compound in the presence of air or other oxidizing medium.

Phosphorus pentoxide is known in two modifications, the first is a crystalline product which sublimates at 250° C. and when heated above this temperature is transformed into the second type which is a soft white amorphous powder volatilizing only at red heat. Phosphoric anhydride is extremely hygroscopic so that it deliquesces in the air and therefore must be stored and shipped in hermetically sealed containers. Advantage is taken of its hygroscopic properties in the chemical laboratory where it is very useful as a desiccating agent.

Phosphoric anhydride dissolves in water with a hissing sound and evolution of heat being converted successively and quickly into meta-, pyro- and finally into orthophosphoric acid, the most important and useful of the oxyacids of phosphorus.

In stating the grade of various phosphatic materials used in the arts and industries the value is usually expressed in terms of P_2O_5 and hence this product is commonly though erroneously known as phosphoric acid.

The Acids of Phosphorus.

There are eight known acids of phosphorus, five of which are formed by the combination of phosphorous and phosphoric anhydrides with certain quantities of water, as shown in the following equations:

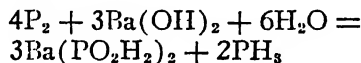
- (1) $P_4O_6 + 2H_2O = 4HPO_2$ = Metaphosphorous acid
- (2) $P_4O_6 + 6H_2O = 4H_3PO_3$ = Phosphorous acid
- (3) $P_2O_5 + H_2O = 2HPO_3$ = Metaphosphoric acid
- (4) $P_2O_5 + 2H_2O = H_4P_2O_7$ = Pyrophosphoric acid
- (5) $P_2O_5 + 3H_2O = 2H_3PO_4$ = Orthophosphoric acid

The other three acids of phosphorus, namely, hypophosphorous, pyrophosphorous and hypophosphoric acid, are not ordinarily prepared by the interaction of water and the oxides of phosphorus.

— OH
— H

Hypophosphorous Acid (H_3PO_2) or $O : P - H$

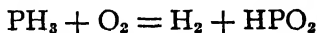
This acid may be obtained by heating a concentrated solution of sodium hydroxide, lime, or barium hydroxide with white phosphorus. Phosphine and the alkali or alkaline earth hypophosphite being formed according to the following equation:



By treating the purified barium salt with sulfuric acid and filtering free hypophosphorous acid is obtained, which can be concentrated under reduced pressure to a syrupy consistency and even to the point where it crystallizes in white scales. At elevated temperatures hypophosphorous acid decomposes into phosphine and phosphoric acid. Hypophosphorous acid and the hypophosphites have a strong affinity for oxygen and hence are powerful reducing agents. Hypophosphorous acid reduces sulfuric acid to sulfur dioxide and the latter gas to elemental sulfur. It also separates such metals as gold, silver and mercury from certain of their salts and hence has a distinct commercial value. The hypophosphites, even those of the heavy metals, are soluble in water but are not very stable, readily changing over to the more highly oxidized phosphites and phosphates.

Metaphosphorous Acid (HPO_2) or $O : P - OH$.

This compound is formed in slender crystals by the partial oxidation of phosphine under reduced pressure according to the following equation.



It is also obtained by the interaction of phosphorous anhydride and a limited amount of water as shown in the first equation on page 23.

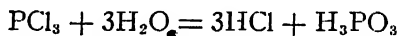
Like the other partially oxidized acids of phosphorus it is rather unstable, going over to phosphorous and phosphoric acids on exposure to air or water. Metaphosphorous acid is of no commercial significance.

Pyrophosphorous Acid ($H_4P_2O_6$) or
$$\begin{array}{c} OH - \\ OH - \end{array} P - O - P \begin{array}{c} - OH \\ - OH \end{array}$$

This acid may be obtained by continuously agitating a mixture of phosphorus trichloride (PCl_3) and phosphorous acid (H_3PO_3) for about 5 hours, keeping the mixture at a temperature of 30° to 40° C. This acid forms needle-like crystals which melt at 38° C. and decompose at 130° C. The acid also decomposes in water to form phosphorous and phosphoric acids. Although pyrophosphorous acid and certain pyrophosphites have been made in the laboratory they have no industrial application.

Phosphorous Acid (H_3PO_3) or $O : P \begin{array}{c} - OH \\ - OH \\ - H \end{array}$

This dibasic acid is formed along with phosphoric and hypophosphoric acids by the slow oxidation of phosphorus in moist air. In the laboratory it can be prepared more conveniently by the adding of phosphorus trichloride to water, taking care to keep the solution cool.

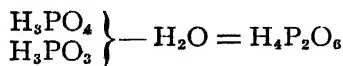


On evaporating this solution in vacuum, the hydrochloric acid is evolved and a colorless crystalline hygroscopic mass of phosphorous acid is obtained which melts at 71° C., but is decomposed at higher temperatures into phosphoric acid and phosphine (PH_3).

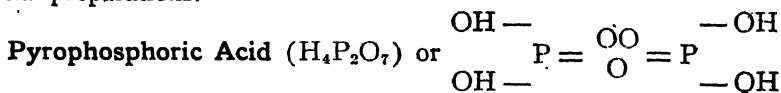
The tendency of phosphorous acid to oxidize to phosphoric makes it a strong reducing agent though not as energetic in this regard as hypophosphorous acid. The salts of phosphorous acid (phosphites) differ from the hypophosphites in not being oxidized in the air. Phosphorous acid is dibasic, forming two series of salts.

Hypophosphoric Acid ($H_4P_2O_6$) or $O : P \begin{array}{c} - OH \\ - OH \end{array} - O - P \begin{array}{c} - OH \\ - OH \end{array}$

This acid may be considered a product formed by the extraction of water from one molecule of phosphoric acid and one molecule of phosphorous acid thus:



It is actually produced, however, along with phosphorous and phosphoric acids by the slow oxidation of phosphorus in moist air. By neutralizing the mixture of acids thus obtained with NaOH, sodium hypophosphite ($\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$) crystallizes out of solution and may be used as the source of the free acid. With a solution of barium chloride, barium hypophosphite is precipitated and on treating this with dilute sulfuric acid, and filtering, hypophosphoric acid may be isolated, concentrated and finally crystallized at temperatures below 30°C . At 70°C . this compound decomposes into phosphorous and phosphoric acids. The hypophosphates are used to a considerable extent in medicinal preparations.

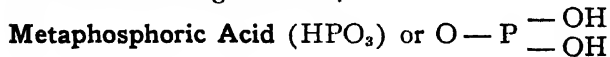


This acid is produced by heating orthophosphoric acid above 210°C ., driving off water thus:



A certain amount of metaphosphoric acid is also formed at the same time, so to prepare the pyrophosphoric acid in a pure state it is customary to heat disodium phosphate until it is changed over into pyrophosphate, then to dissolve this salt in water and precipitate with a soluble lead compound. The lead in turn is precipitated with H_2S and the solution filtered off and concentrated in vacuum until a white crystalline mass of pyrophosphoric acid is obtained. On addition of water it readily goes back to phosphoric acid.

Pyrophosphoric acid is tetrabasic but only two series of salts are known, namely the di- and tetrabasic. These are quite stable and have some industrial significance.



If pyrophosphoric acid is heated to redness water is driven off and metaphosphoric acid is produced thus:



This compound may also be obtained by adding the theoretical quantity of water to phosphoric anhydride. Thus:



Metaphosphoric acid is a transparent glassy mass which melts at 61°C . and sublimes at white heat without decomposition. It is the most

stable of the oxyacids of phosphorus at high temperatures, but goes back to orthophosphoric acid when dissolved in water or exposed to the atmosphere. The salts of metaphosphoric acid (metaphosphates) are formed by driving off water from the primary phosphates. On heating these compounds with water, however, the reverse reaction gradually takes place and orthophosphates are again produced.

Metaphosphoric acid and the metaphosphates have as yet but little commercial significance.

— OH
— OH
— OH

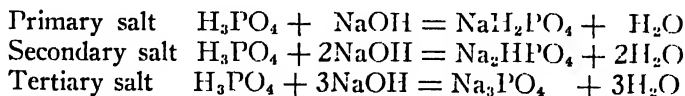
Orthophosphoric Acid (H_3PO_4) or O : P

This acid in combination with lime is widely distributed in nature. The crystalline mineral apatite of which two types ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) and $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$) exist, is found as veins in igneous rocks, and from this mineral, no doubt, are derived the amorphous phosphates which are concentrated in immense deposits in various parts of the world.

Phosphoric acid is by far the most important of the oxyacids of phosphorus and the orthophosphates are used as a basis in the preparation of elemental phosphorus as well as all other phosphorus compounds.

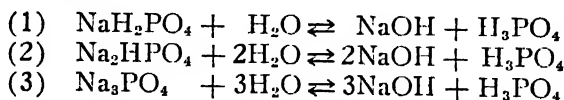
When free from water phosphoric acid forms colorless prismatic crystals which melt at 386°C . and readily deliquesce in the air. As ordinarily prepared, however, the acid is a colorless thick syrupy liquid with strongly acid properties, up to the point where one atom of hydrogen is replaced), readily attacking most metals with the evolution of hydrogen and the formation of the corresponding phosphate.

Orthophosphoric acid being tribasic gives rise to three series of salts as illustrated in the following reactions :



The normal sodium salt gives an alkaline solution, the secondary salt a solution which is practically neutral or slightly alkaline, while the primary salt is quite acid to litmus and phenolphthalein.

This behavior is due to the hydrolysis of these salts in accordance with the following equations :

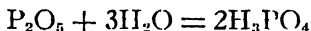


Since sodium hydroxide is a more powerful base than phosphoric acid is an acid, solutions of the normal salt act as if an excess of alkali

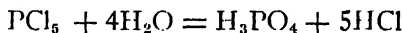
were present, while in the case of the secondary salt the greater strength of the base is offset by the fact that the proportion of acid hydrogen to base in the hydrolized solution is in the ratio of 3 to 2. Finally in the primary salts the relation of acid hydrogen to base is 3 to 1, which results in solutions distinctly acid in nature.

When heated to 300° to 400° C. water is evolved and phosphoric acid is converted into pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$) and if the temperature is carried to 400° C. a further quantity of water is driven off and the whole is converted into a vitreous mass of metaphosphoric acid (HPO_3).

Phosphoric acid may be prepared in the laboratory by dissolving phosphoric anhydride in hot water, thus



or by decomposing phosphorus penta-chloride in water.



Industrially it is prepared either by the action of sulfuric acid on bones or phosphate rock, or by heating mixtures of natural phosphates and silica under reducing conditions. The commercial methods of preparation are discussed in detail further on in this publication.

Phosphoric acid and its compounds have a wide application in the arts and industries, but by far the greatest use is in the production of phosphatic fertilizers.

PHOSPHORIC ACID IN ANIMAL METABOLISM.

While this book is chiefly taken up with the sources of phosphoric acid and methods of preparing this acid and its various compounds of more or less commercial importance, the function of phosphoric acid, which is of the most vital concern to man is the part it plays in animal metabolism.

The term metabolism in the broader sense of the word may be used to designate the chemical changes taking place in the utilization of food by man and animals in the life process. The products of metabolism, therefore, include not only those absorbed in building up the animal body but those contained in the solid, liquid and gaseous excreta.

Metabolism includes two distinct processes, namely, anabolism by which simple molecules are built up into more complex organic compounds, and katabolism whereby the more complex compounds are broken down into simpler molecules. Since the life process is one of continual oxidation the greater tendency is towards the formation of the less complex products.

Metabolism, however, is not a simple oxidation or burning process but takes place in gradual steps in the nature of cleavages and hydrations and it is the products of these changes which unite directly with oxygen.

The rôle of phosphorus in animal metabolism has been so ably handled by Forbes and Keith ²⁴ (who include in their book a very complete list of references on various phases of the subject) that only a brief summary of some of the more important points is included here. For details, therefore, the reader is referred to the carefully prepared and excellent monograph by the authors mentioned above.

Since phosphorus in both organic and inorganic combination is an essential constituent of the bones, brain, blood, and tissue of men and animals, our daily diet must consist of food containing sufficient quantities of this element to permit of normal growth in the young and maintain the health and strength of the adult.

According to Forbes and Keith ²⁵ the phosphorus in both animal and vegetable matter is in a highly oxidized condition and probably exists in the form of organic and inorganic compounds of orthophosphoric acid. They conclude, therefore, that there is probably no significant change in the state of oxidation of the phosphorus during metabolism although Heffter ²⁶ observed some capacity of animals to oxidize the less completely oxidized phosphorus compounds.

Gilbert and Posternak ²⁷ sum up the total P_2O_5 content of the human body as being 30 to 40 grams at birth and about 1600 grams at middle age. Of this amount 1400 grams are contained in the bones, 130 grams in the muscles, 12 grams in the brain, 10 grams in the liver, 6 grams in the lungs and about 4 in the blood.

In the following table (Table I), compiled by Beaunis and quoted by Forbes and Keith, ²⁸ the ash analyses of various animal tissues and products are given. The prominence of phosphoric acid in bone, muscle, brain and liver is very marked, being approximately 50 per cent of the ash of these parts.

While phosphoric acid in both organic and inorganic combination is a constituent part of the animal body, this compound apparently performs certain other necessary functions in the life process independent of its absorption and retention by the bones, organs and tissues.

²⁴ Phosphorus Compounds in Animal Metabolism. Technical Bull. No. 5 Ohio Exper. Station (1914).

²⁵ Loc. cit., pp 32, 45, 182.

²⁶ Die Ausscheidungskörper fremder Substanzen im Harn, I Teil Anorganische Verbindungen, Ergebnisse d. Physiol. 2 I Abt. 95-129 (1903).

²⁷ Weber, Die Phosphorthérapie vom Standpunkte des Stoffwechsels aus betrachtet, Aertzliche Rundschau (München) 15, 398-402; 411-415 (1905).

²⁸ Loc. cit., p. 105 (1914).

TABLE I
ASH ANALYSES OF VARIOUS PARTS OF THE ANIMAL BODY AND ITS PRODUCTS (PER CENT)

Ingredients	Bone	Calf Muscles	Brain	Liver	Lungs	Blood	Serum	Urine	Milk	Bile	Excrements
Sodium chloride	10.59	4.74	13.0	58.81	72.88	67.26	10.73	27.70	4.63
Potassium chloride
Soda	2.35	10.69	14.51	19.5	4.15	12.93	1.33	26.33	36.73	5.07
Potash	34.40	34.42	25.23	1.3	11.97	2.95	13.64	21.44	4.80	6.10
Lime	37.58	1.99	.72	3.61	1.9	1.76	2.28	1.15	18.78	1.43	26.40
Magnesia	1.22	1.45	1.23	.20	1.9	1.12	.27	1.34	.87	.53	10.54
Ferric oxide	2.74	3.2	8.37	.2610	.23	2.50
Chlorine	2.58
Fluorine	1.66
Phosphoric acid	53.31	48.13	48.17	50.18	48.5	10.23	1.73	11.21	19.00	10.45	36.03
Sulfuric acid75	.92	1.4	1.67	2.10	2.64	6.39
Carbonic acid	5.47	1.19	4.40	11.26
Silicic acid	0.81	.12	.27	0.20	4.0636	3.13

Loeb²⁰ conducted certain experiments on dogs which indicated that phosphorus is utilized in the preparation of the digestive juices. Such phosphorus may subsequently be almost entirely excreted and thus be utilized only indirectly in the building up or maintenance of the animal's health and strength.

Löb²⁰ demonstrated that phosphates play an important part in the digestion or utilization of sugar, and that glycolysis was favored by the presence of phosphate ions.

Forbes and Keith²¹ conclude that the available data show that phosphates stand in significant relation to the digestion of food and that their excretion into the alimentary tract is of necessary consequence. Moreover, the fact that both phosphoric and sulfuric acids are prominent among the normal products of protein katabolism makes it inevitable that the excreta of man and animals contain appreciable quantities of phosphates.

Another function which phosphates play in the life process is that of helping to maintain the body fluids in a neutral or slightly alkaline state. According to Henderson²² the phosphoric acid in such fluids is in the form of mono- and disodium phosphates and that mixtures of these salts in solution have greater power than any known salts for balancing either one another or any acid or base added thereto. He maintains that solutions containing these two salts will not exhibit an acid reaction until all of the disodium phosphate has been changed to the mono salt and that an alkaline reaction can only be obtained by completely converting the mono salt into disodium phosphate.

It has been established beyond question that a diet low in phosphorus compounds or that phosphates fed under conditions which hinder their efficient utilization bring about harmful results.

White rice for instance does not contain as much phosphorus as the adult human being requires, whereas red or unpolished rice contains more than sufficient. We store more phosphorus from whole wheat bread than from white bread.

Young flesh eating animals suffer malnutrition of the bones if they are fed on meat alone.

The deposit of calcium phosphate in the bones is hindered by inorganic acids and acid salts as well as by calcium precipitating ions other than phosphorus. Lime in some form along with phosphoric acid is essential for the efficient utilization of phosphorus by men and animals.

²⁰ Zeit. Biol., 55 (N.F. 37), 167-235 (1910).

²⁰ Biochem. Zeit., 32, pp. 43-58 (1911).

²⁰ Loc. cit., p. 186 (1914).

²¹ Jour. Physiology, Vol. 15, pp. 257-271 (1906); *Ibid.*, Vol. 21, pp. 173-179 and 427-448 (1908).

Forbes and Keith,³³ in summing up the relation of common foods to animal metabolism, state that protracted feeding of rations poor in both phosphorus and lime may seriously weaken the bones, whereas food high in these ingredients will greatly strengthen them. These authorities further state that while calcium phosphate in the diet does not greatly influence gain in body weight it is readily deposited in the bones especially within the narrow spaces, increasing the density and strength of these supporting structures.

Much time has been devoted to experiments conducted with a view to determining the relative effectiveness of organic and inorganic phosphorus in the diet of men and animals.

The fact that practically all food products (with the exception of eggs) contain both organic and inorganic phosphorus and that bones are largely made up of phosphate of lime led to investigations on the practicability of substituting a larger proportion of inorganic, and cheaper salts of phosphoric acid for the complex and more expensive organic forms contained in certain food products.

While this problem might appear at first sight to be relatively simple, direct experimentation has shown that there are so many factors involved that it is difficult to draw very definite conclusions and there never has been a unanimous opinion as to the facts.

It has never been definitely established that organic phosphorus is absolutely essential to animal life, nor is there complete proof that inorganic phosphorus can serve all the purposes for which the animal needs this element.

There is much evidence that with some species, organic phosphorus compounds are more readily utilized than inorganic forms, but on the other hand it seems likely that the many demonstrations of superior nutritive value of organic over inorganic phosphorus compounds have been influenced by other beneficial substances (such as vitamins, etc.) associated with them in natural foods or contained as impurities in the organic phosphorus compounds isolated for experimental purposes.

Forbes and Keith³⁴ conclude, however, that one point at least has been definitely established, namely, that an amount of organic phosphorus in food products equal to a very small part of the total is sufficient for growth and reproduction provided that inorganic phosphorus is present in sufficient quantities to supply the balance.

In the tables 1a and 1b given on page 33, compiled by Forbes, Beegle and Mensching,³⁵ are given the mineral constituents of certain

³³ Loc. cit., p. 395 (1914).

³⁴ Loc. cit.

³⁵ Mineral and Organic Analyses of Foods. Ohio Agr. Exper. Sta. Bull. 255, pp. 211-231 (1913).

will known feeds and the percentage of organic and inorganic phosphorus which such products contain. It will be noted that with the exception of milk products (skimmed milk and whey) malt sprouts, peanuts and bone and tankage, organic phosphorus compounds predominate over the inorganic forms.

Unquestionably phosphate of lime is utilized by the young as well as the adult animal and certain organic wastes or by-products such as tankage, blood, bone, fish and cottonseed meal, all of which contain nitrogen and phosphoric acid, are now being extensively employed as stock and poultry feed. At one time such materials were used largely in the preparation of mixed fertilizers, but it is now realized that the protein content of these products can be utilized immediately and far more economically by feeding them directly to the animal than by breaking down this protein in the soil only to build it up again through the medium of plant life.

Because of their high protein content, most of these materials are classed as concentrated stock feeds, but from a fertilizer standpoint such products are low grade because protein is only valued for its content of available phosphoric acid and nitrogen both of which can be furnished more cheaply by the application of inorganic salts carrying high percentages of these ingredients.

Within the past few years there has been an appreciable tonnage of phosphatic limestone used as chicken grit. This is employed as a substitute for oyster shell and ground bone since it contains the essential constituents of both products (lime and carbonic and phosphoric acids) and answers admirably the requirements of the gizzard for a mineral to grind or prepare the poultry feed. There appears to be considerable evidence that such a mineral is effective in furnishing lime and phosphoric acid for building up the bones of the birds and increasing egg production.

THE RÔLE OF PHOSPHORIC ACID IN AGRICULTURE

Because phosphoric acid is the main fertilizer element used in American agriculture and the predominating ingredient of nearly all mixed fertilizers, it is rather popularly supposed that plants require larger quantities of phosphoric acid than of either potash or nitrogen. Analyses of the more common and extensively grown crops, however, as reported by a number of investigators,³⁰ show conclusively that such is not the case.

³⁰ Hopkins, C. G., *Soil Fertility and Permanent Agriculture*, pp. 154-155 (1910); Hall, A. D., *Fertilizers and Manures*, p. 22 (1908); Thorne, C. E., *Farm Manures*, pp. 39-42 (1913); Van Slyke, L. L., *Fertilizers and Crops*, p. 597 (1917); Burkett, C. W., *Soils*, p. 83 (1907); Patterson, H. J., *Bull. 94, Pennsylvania Dept. of Agriculture*, pp. 10-14 (1902).

TABLE Ia

MINERAL ELEMENTS OF LEGUMINOUS SEEDS, NITROGENOUS CONCENTRATES AND ANIMAL PRODUCTS USED AS FEED (PARTS PER 100 OF DRIED SUBSTANCE)

Class of Feed	Potas- sium	Sodium	Calcium	Magne- sium	Sulfur	Chlorine	Phosphorus (Total)	Phosphorus (Inorganic)	Phosphorus (Organic)
Soy beans	2.095	.380	.230	.244	.444	.025	.649	.017	.632
Navy beans	1.390	.086	.235	.206	.224	.047	.429	.088	.341
Cowpeas	1.636	.189	.117	.243	.280	.047	.532	.023	.509
Peanuts061	.563	.068	.180	.254	.024	.399	.049	.350
Linseed oil meal...	1.224	.282	.403	.544	.455	.095	.786
Cottonseed meal...	1.811	.283	.291	.599	.536	.042	1.479	.078	1.401
Milk (skim)	1.272	.488	1.336	.146	.357	.953	.979	.551	.428
Whey	2.762	.459	.721	.138	.139	1.948	.640	.402	.238
Mutton624	.214	.006	.062	.607	.235	.474	.230	.244
Eggs206	.389	.250	.059	.762	.621	.856	trace	.856
Tankage601	1.830	3.242	.159	.669	2.687	1.789
Bone flour065	.091	23.990	1.160	14.940	14.940
Blood (swine)	1.040	1.370	.031	.028	.647	1.200	.280	.076	.204
Black albumen027	1.247	.039	.011	.820	1.550	.122	.037	.085

TABLE Ib

MINERAL ELEMENTS OF CEREAL PRODUCTS (PARTS PER 100 OF DRY SUBSTANCE)

Grain or Its Product	Potas- sium	Sodium	Calcium	Magne- sium	Sulfur	Chlorine	Phosphorus (Total)	Phosphorus (Inorganic)	Phosphorus (Organic)
Wheat	0.590	.035	.056	.142	.224	.095	.425	.038	.387
Wheat flour058	.127	.022	.019	.168	.081	.102	.017	.085
Wheat bread156	.583	.038	.004	.198	.958	.135	.043	.092
Wheat bran	1.464	.223	.139	.590	.297	1.000	1.233	.034	1.199
Wheat middlings ..	1.147	.186	.108	.430	.263	.029	.984	.069	.915
Wheat germ323	.788	.078	.372	.355	.077	1.147
Wheat gluten007	.031	.085	.049	1.000	.055	.220	.037	.183
Red dog flour425	.733	.134	.324	.285	.156	.928	.098	.830
Corn396	.030	.014	.126	.171	.073	.303	.028	.275
Corn meal (bolted)	.192	.113	.015	.122	.122	.070	.264	.019	.245
Corn bran410	.000	.030	.088	.124	.052	.156	.031	.125
Pearl hominy153	.000	.005	.036	.182	.052	.111	.019	.092
Gluten feed272	.461	.268	.239	.636	.098	.589	.106	.483
Distillers' grains (corn)014	.154	.047	.054	.509	.065	.314	.056	.258
Distillers' grains (rye)045	.077	.142	.195	.408	.028	.458	.018	.440
Brewers' grains185	.278	.169	.172	.419	.062	.503	.162	.341
Malt sprouts219	1.458	.159	.194	.864	.389	.746	.471	.275
Oats460	.184	.112	.130	.214	.077	.434	.059	.375
Kafir corn288	.066	.013	.142	.186	.117	.271	.012	.259
Rice040	.032	.009	.028	.114	.040	.104	.003	.101
Rice polish	1.279	.124	.030	.741	.189	.151	1.684	.028	1.656

TABLE Ic
APPROXIMATE AMOUNTS OF NITROGEN, PHOSPHORIC ACID AND POTASH IN AVERAGE
YIELDS OF CERTAIN COMMON CROPS (VAN SLYKE)³⁷

Crop	Portion of Crop	Yields per Acre	Quantities of Fertilizer Elements Removed		
			Nitrogen (N)	Phosphoric Acid (P_2O_5)	Potash (K_2O)
			Lbs.	Lbs.	Lbs.
Corn	Grain	25 bus.	23.2	9.1	5.5
	Stalks	1,500 lbs.	15.0	4.5	21.0
	Cobs	250 lbs.	1.0	0.2	1.1
	Total		39.2	13.8	27.6
	Green forage ..	20,000 lbs.	60.0	26.0	66.0
Wheat	Grain	25 bus.	30.0	12.8	6.0
	Straw	2,500 lbs.	12.5	3.8	15.0
	Total		42.5	16.6	21.0
Rye	Grain	20 bus.	19.1	9.8	6.7
	Straw	2,000 lbs.	10.0	6.0	17.0
	Total		29.1	15.8	23.7
	Green forage ..	15,000 lbs.	67.5	30.0	97.5
Oats	Grain	25 bus.	16.0	6.5	4.8
	Straw	1,250 lbs.	8.0	2.5	15.6
	Total		24.0	9.0	20.4
	Green forage ..	12,000 lbs.	72.0	18.0	54.0
Barley	Grain	25 bus.	21.0	9.0	6.0
	Straw	1,600 lbs.	9.6	3.2	17.6
	Total		30.6	12.2	23.6
	Green forage ..	10,000 lbs.	40.0	15.0	50.0
Buckwheat ...	Grain	20 bus.	15.0	6.0	3.0
	Straw	5,000 lbs.	62.5	7.5	57.5
	Total		77.5	13.5	60.5
	Green forage ..	10,000 lbs.	40.0	8.0	35.0
Cotton ³⁸	Lint	1,000 lbs.	3.0	0.9	4.8
	Seed	2,000 lbs.	63.0	25.2	24.7
	Stalks	4,000 lbs.	102.2	41.2	76.7
	Total		168.0	67.3	106.2
Millet	Green forage ..	20,000 lbs.	60.0	20.0	100.0
Sorghum	Green forage ..	20,000 lbs.	60.0	24.0	60.0

³⁷ Fertilizers and Crops, p. 597.

³⁸ Maximum amounts of N, P_2O_5 , and K_2O removable by a single cotton crop. Hopkins, C. G., Soil Fertility and Permanent Agriculture, p. 154 (1910).

In Table Ic are given the quantities of nitrogen, phosphoric acid and potash which are removed by an average crop of forage, cereals, and cotton.

An inspection of Table Ic will show that in every instance without exception greater quantities of nitrogen and potash than of phosphoric acid are removed by the crops listed.

If we regard the function of phosphates as merely that of supplying phosphoric acid directly to the plant it would seem that fertilizers in which available potash and nitrogen predominate should prove much more effective in increasing crop yields than those carrying larger proportions of phosphoric acid. But when we consider on the other hand the composition of typical agricultural soils from many parts of the world in respect to these three fertilizer ingredients we find that in the majority of cases their content of phosphoric acid is far less than that of potash and frequently is considerably below their nitrogen content.³⁹ Probably the following table as given by Van Slyke⁴⁰ is as typical as any of the average composition of good productive soils.

TABLE II

PROPORTIONS OF TOTAL NITROGEN, PHOSPHORIC ACID, POTASH AND LIME IN FIRST NINE INCHES OF GOOD PRODUCTIVE SOILS

Constituent	Per Cent	Pounds in One Acre to a Depth of 9 Inches
Nitrogen (N)	0.10 to 0.30	2,500 to 7,500
Phosphoric acid (P_2O_5)07 to 0.25	1,750 to 6,250
Potash (K.)	1.00 to 2.00	25,000 to 50,000
Lime (CaO)	0.28 to 2.10	7,000 to 52,500

Not only is phosphoric acid more likely to be deficient in agricultural soils than either potash or nitrogen, but in the use of commercial fertilizers containing readily soluble phosphates it is a well known fact that such phosphates soon revert in the soil to less soluble compounds of phosphoric acid.⁴¹ While it is generally conceded that reverted phos-

³⁹ Burkett, C. W., *Soils*, pp. 83-84 (1907); Hopkins, C. G., *Soil Fertility and Permanent Agriculture*, pp. 58-106 (1910); Hilgard, E. W., *Soils*, pp. 311-412 (1910); Schutt, F. T., *Dominion Exp. Farms Report*, p. 169 (1897); Whitney, Milton, *Bull. No. 57, Bureau of Soils*, pp. 65-127 (1909); Lyon, Fippin and Buckman, *Soils*, pp. 33, 37-38, 59-60, 66-72 (1915); Clark, F. W., *Data of Geochemistry Bull.* 491, U. S. Geol. Survey, p. 486 (1911); Kedsie, R. C., *Mich. Exp. Sta. Bull.* 99, pp. 6-15 (1893); Fraps, G. S., *Texas Exp. Sta. Bull.* 99, pp. 14-41 (1907); Selby and Ames, *Ohio Exp. Sta. Bull.* 150, pp. 94-141 (1904); Roberts, I. P., *Fertility of the Land*, p. 13 (1897); Goesman and Haskins, *Mass. Exp. Sta. Bull.* 117, p. 19 (1907).

⁴⁰ Van Slyke, *Fertilizers and Crops*, p. 115 (1917).

⁴¹ Liebig, J., *Organic Chemistry in its application to Agriculture and Physiology*, p. 184 (1840); Schreiner and Failer, *Bull.* 32, Bureau of Soils, U. S. Department of Agri. (1906); Hall, A. D., *The Soil*, pp. 219-222 (1908); Cameron and Bell, *Bull.* 41, Bureau of Soils, pp. 12-26 (1907); Sutherst, W. F., *Reversion of superphosphate of Lime in the Soil*, *Chem. News*, 86, p. 170 (1902).

phates are still available to plants it is hardly to be expected that they would yield soil solutions as concentrated with respect to phosphoric acid as the original water-soluble salt.⁴²

While it must be admitted that the favorable results obtained after years of experience with materials in which phosphoric acid has predominated over both potash and nitrogen point strongly to the advisability of using fertilizers having high proportions of this fertilizer ingredient, nevertheless, the extensive use of phosphates in this country is also due in a large measure to the fact that we have such immense resources of phosphoric acid and therefore under normal conditions this fertilizer ingredient is cheaper than any other.

Laboratory, greenhouse, and field studies have shown that while phosphatic fertilizers undoubtedly furnish a certain amount of more quickly available phosphoric acid than that already in the soil they also perform a number of other important functions which have both direct and indirect effects upon the soil and the crop. Soluble phosphates favor the rapid development of the young seedling by stimulating the growth of their roots, and therefore their early application often enables a plant to withstand adverse climatic conditions encountered later in the season. It is also generally believed that the liberal use of phosphates tends to hasten the early maturity and ripening of crops: an effect due to the close relationship which phosphoric acid bears to seed production.⁴⁴ In climates where the crop season is of relatively short duration and in sections where truck is produced for the early market, the quick maturity of crops is often the main factor to be considered and therefore success may largely depend on the liberal use of readily available phosphatic fertilizers. The tendency of phosphoric acid to increase the proportion of grain to stalk is one of its most important functions in the growing of cereal crops. This action of phosphoric acid is directly opposite to that of nitrogenous fertilizers, which tend to delay maturity and promote the growth of stalk and forage at the expense of the fruit. The presence of phosphoric acid is also essential for the formation of chlorophyll.⁴⁴ Other effects which soluble phosphates have upon the soil and indirectly upon the crop are the altering of the solubility of other soil constituents,⁴⁵ influencing the growth of soil bacteria and nullifying the injurious effect of certain toxic organic bodies formed in

⁴² Gile and Carrero, Bull. #25, Porto Rico Exp. Sta. (1918).

⁴³ Hall, A. D., *Fertilizers and Manures*, p. 136 (1911); Van Slyke, L. L., *Fertilizers and Crops*, pp. 70-71 (1917); Patterson, H. J., Bull. 94, Pennsylvania Dept. of Agri., p. 9 (1902); Loew, Oscar, Bull. 18, Division of Vegetable Physiology and Pathology, U. S. Dept. Agri., p. 14 (1899).

⁴⁴ Loew, Oscar, Bull. 18, Division of Vegetable Physiology and Pathology, p. 14 (1899).

⁴⁵ Cameron, F. K., *The Soil Solution*, p. 52 (1911); Cameron and Bell, Bull. 41, Bureau of Soils (1907).

the soil.⁴⁶ Also protoplasm, that essential part of both animal and vegetable life, can exist only if the plant is supplied with sufficient phosphoric acid to enable it to function properly.

SOURCES OF PHOSPHORIC ACID AND THEIR CLASSIFICATION.

While no very strict line can be drawn between soluble and insoluble phosphates or between available and unavailable forms of phosphoric acid or even between natural and manufactured phosphatic fertilizers, nevertheless for convenience the following three broad classifications are made, based partly on the relative solubility of such phosphates and partly upon their mode of occurrence and their chemical and physical properties.

(1) The natural phosphates including raw bone, guano, apatite and phosphorite or phosphate rock, all of which with the exception of certain types of guano are nearly insoluble in water and are but slowly available under soil conditions.

(2) The so-called available phosphates which are the products or by-products of various industrial processes and while very sparingly soluble in water, dissolve readily in certain conventional laboratory solutions. These phosphates include steamed or degreased bone, basic slag, di-calcium phosphate and a number of manufactured materials which yield their phosphoric acid upon treatment with neutral ammonium citrate solution or 2 per cent citric acid.

(3) Water soluble phosphates or those which dissolve most readily and have as a rule the quickest effect upon crop yields. The chief products under this classification are ordinary acid phosphate, double superphosphate and ammonium phosphate all of which are main products of industrial processes.

The phosphoric acid content of typical phosphate materials both natural and manufactured are given below in Table III.

The Natural Phosphates.

The natural or relatively insoluble phosphates represent the raw materials from which the plant must draw its phosphoric acid, whether they are applied in their natural state directly to the soil with very little preliminary preparation, or so manipulated in the factory as to yield phosphatic compounds of entirely different composition. From the natural phosphates are also produced elemental phosphorus, the acids of

⁴⁶ Schreiner, O., and Skinner, J. J., Bull. No. 77, Bureau of Soils (1911); Skinner, J. J., and Noll, C. F., Field Tests of Fertilizer Action on Soil Aldehydes, Jour. Amer. Soc. of Agron., Vol. 8, p. 273 (1916); Skinner, J. J., Soil Aldehydes, Jour. of Franklin Institute, Aug. to Dec. (1918).

TABLE III
COMPOSITION OF NATURAL AND MANUFACTURED PHOSPHATES USED DIRECTLY OR INDIRECTLY IN AGRICULTURE

Phosphatic Material	Location	Nitrogen (N)	Silica or Insoluble (SiO ₂)	Oxide of Iron and Aluminium (Fe ₂ O ₃ - Al ₂ O ₃)	Calcium Fluoride (CaF ₂)	Carbonate of Lime (CaCO ₃)	Phosphoric Acid (P ₂ O ₅)	Tricalcium Phosphate (Ca ³⁺ (PO ₄) ₂)
Apatite	Bohemia	5.26	8.54	30.59	66.79
Apatite	Canada	3.7 to 8.9	0.7 to 1.0	3.0 to 7.3	0.0 to 8.0	34.4 to 40.0	78.6 to 86.8
Apatite	Norway	3.62	1.37	2.62	0.29	39.44	86.10
Coprolites	Bohemia	6.99	15.25
Coprolites	France	6.0 to 17.0	12.0 to 21.0	26.3 to 46.0
Coprolites	Great Britain	3.00	4.4 to 13.0	3.0 to 6.0	2.3 to 24.0	15.4 to 34.0	33.6 to 77.7
Guano	S. Africa	1.4 to 8.9	3.25	11.2 to 24.5	24.4 to 55.4
Guano	S. America	1.3 to 14.4	1.0 to 2.0	0.0 to 14.0	9.8 to 17.5	21.3 to 38.3
Guano	Australia	7.54	0.97	6.97	7.30	15.94
Guano (Bat)	Italy	5.72	trace	5.02	10.95
Guano (Bat)	Porto Rico	8.35	1.59	7.57	16.52
Guano (In crusts)	Sporadic Isles	40.12	87.58
Guano (In crusts)	W. Indies	0.45	0.4 to 9.3	24.4 to 40.5	53.2 to 60.8
Guano (Phospho)	S. Africa	0.43	6.68	14.60
Guano (Phospho)	Asia	0.8 to 1.4	1.48	6.23	26.2 to 31.2	57.3 to 68.0
Guano (Phospho)	Australia	0.4 to 1.3	0.8 to 3.1	trace to 2.6	4.3 to 4.6	23.6 to 35.2	51.4 to 76.9
Guano (Phospho)	Pacific Ocean Isles	0.3 to 1.3	0.2 to 0.3	0.8 to 1.0	4.5 to 16.5	17.7 to 40.3	38.6 to 88.0
Guano (Phospho)	Mexico & West In- dies	0.1 to 0.4	trace to 5.8	3.8 to 12.8	11.6 to 39.7	25.3 to 86.7
Phosphatic chalk	Belgium	2.4 to 2.9	7.04	22.2 to 27.3	48.4 to 59.5
Phosphorites	Algeria (Africa)	0.5 to 1.0	0.0 to 22.8	26.3 to 30.4	57.4 to 66.4
Phosphorites	Morocco (Africa)	1.2 to 2.6	0.7 to 1.6	5.2 to 9.4	6.4 to 10.0	32.8 to 35.2	71.6 to 76.7
Phosphorites	Tunis (Africa)	6.0	1.0 to 2.0	6.6	11.5 to 14.0	27.5 to 31.2	60.0 to 68.0
Phosphorites	Egypt (Africa)	3.0 to 9.9	1.0 to 2.3	9.3 to 11.3	28.0 to 32.9	61.2 to 71.8
Phosphorites	Christmas Isle (Asia)	1.93	3.44	4.82	39.70	83.53
Phosphorites (White)	Ocean Isle (Pacific)	0.42	1.00	4.91	38.73	84.65
Phosphorites	Podolia (Russia)	6.92	34.00	74.23

Phosphorites	2.21	9.10	32.25	70.42
Phosphorites	1.3 to 2.2	10.3 to 13.3	29.5 to 38.9	59.6 to 85.0
Phosphorites Black Rock...	2.5 to 9.5	23.0 to 28.0	53.0 to 64.0
Phosphorites Hard Rock...	3.0	3.63	36.39	83.14
Phosphorites Land Pebble...	1.0 to 4.0	2.0 to 5.0	30.0 to 34.0	69.0 to 78.0
Phosphorites Soft Phosphate	25.0 to 27.0	54.5 to 58.8
Phosphorites Brown Rock...	2.5 to 5.0	30.0 to 35.0	69.0 to 80.0
Phosphorites Nodules	1.0 to 4.0	11.0 to 25.0	25.0 to 28.0	57.0 to 64.0
Phosphorites Brown Rock...	3.0 to 8.0	0.0 to 10.0	30.0 to 38.0	69.0 to 87.0
Phosphorites Blue Rock...	2.5 to 7.0	0.0 to 2.0	27.0 to 32.0	62.0 to 73.0
Phosphorites White Rock...	1.5 to 3.5	32.0 to 38.0	73.0 to 87.0
Phosphorites Oolitic Black	0.7 to 1.6	3.8 to 13.6	27.0 to 36.5	62.0 to 83.0
Fresh Bone	4.00	5.00	22.30	48.70
Bone Ash	4.14	5.28	35.38	76.65
Bone (fat extracted)	4.14	5.24	21.68	46.50
Bone or animal charcoal	1.12	0.37	8.00	31.99	73.10
Tankage (high grade)	8.20	3.70
Tankage (low grade)	5.00	11.40
Basic slag	18.0 to 20.0
Acid phosphate	14.0 to 18.0
Di-calcium phosphate	52.2
Double acid phosphate	45.0 to 50.0
Ammon. phosphate	10.8	55.5

phosphorus and the various salts of phosphoric acid which are annually coming to have a greater commercial significance and a wider industrial application.

While finely ground (but otherwise untreated) natural phosphates undoubtedly have an agricultural value and are still used for fertilizer purposes to a limited extent, most of them are generally regarded as inferior to the factory manipulated phosphates the nature of which has been altered by the application of high temperature or treatment with various chemical reagents.

Raw or Green Bone.—The first use of raw or green bone for fertilizer purposes is so ancient as to be lost in antiquity. Long before their composition was suspected they were employed in their natural state (frequently not even crushed) to increase crop yields, and later when the fertilizer value of phosphoric acid was established and the nature of bones determined by chemical analysis the demand for bones became so great that old battle fields were plowed up and ancient cattle ranges sought for what was then considered one of the most valuable of phosphate fertilizers.

While raw bones differ considerably in composition depending on their source, age and the natural agencies which have been at work, upon them, as ordinarily collected they contain from 20 to 22 per cent of phosphoric acid and from 5 to 7 per cent of nitrogen.

The term raw bone, however, is rather an indefinite one since it includes not only bones from recently slaughtered animals but also those which have been weathered or buried for long periods of time. Both the nature and agricultural efficiency of these two extremes differ greatly and large quantities of bones are now seldom purchased without knowing their source and chemical composition.

In addition to large amounts of water, fresh or green bones contain over 40 per cent of organic matter, part of which is of such a character as to delay considerably the decomposition of the bone under soil conditions. The approximate composition of such bones is as follows:

Moisture	34.00	per cent
Mineral matter (ash).....	23.00	" "
Fats	20.00	" "
Albuminoids	21.00	" "
Undetermined organic matter.....	2.00	" "

The mineral matter or ash of average bone has the following composition:

Calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$)...	87.00	per cent
Calcium carbonate (CaCO_3).....	12.00	" "
Silica (SiO_2), Fluorine (F), etc....	1.00	" "

The albuminoids in bone consist chiefly of ossein a gelatinous material containing nearly 18 per cent of nitrogen and valuable for the manufacture of glue. While the albuminoids when moistened decompose or putrefy very readily, their presence in fresh bone renders the latter very difficult to grind. The fat or grease in fresh bones, on the other hand, retards their decomposition in the soil and hence lessens their value for agricultural purposes. Raw bones which have been weathered contain far less moisture and organic matter than fresh bone and can as a rule be much more readily ground. The availability of the phosphoric acid contained therein, however, is not as high as that in processed or degreased bone which is discussed further along under the heading of "Available Phosphates."

In the light of our present knowledge raw bone is not an efficient phosphate fertilizer and it has been found to be far more economical to extract from such material the by-products of gelatine and fat and use as a fertilizer the degreased residue which is easily ground and readily available to crops.

Bone charcoal and bone ash hardly belong under the classification of natural phosphates because they have been processed to a certain extent by artificial means. As far as their agricultural availability is concerned, however, they should be included among the relatively insoluble phosphates since they show a solubility in conventional media but little greater than that of finely ground phosphate rock.

The former material (bone charcoal) is the residue remaining after bones have been submitted to destructive distillation in air tight retorts and the volatile constituents driven off or decomposed. The organic matter which remains is largely carbon. Bone black is produced primarily for the purification and clarification of oils and sugar juices and only after its activity for these purposes is largely spent does it enter into the fertilizer industry. Its solubility in water and citrate solutions is very slight and while the nitrogen which it takes up in the purification of sugar adds somewhat to its value as a fertilizer, the general practice is to treat spent bone black with sulfuric acid and convert its P_2O_5 into a water soluble form. Bone black varies greatly in composition depending on how often it has been used and revived. Fritsch ⁴⁷ gives the following analyses of several samples of bone black before and after being used in the refining of sugar.

The manufacture, use and revivification of bone black is treated more fully in a subsequent chapter under the heading of "Phosphoric Acid and Phosphates in Sugar Refining."

⁴⁷ Mfr. of Chem. Manures, p. 192 (1911).

TABLE IV
ANALYSES OF FRESH, USED AND SPENT BONE BLACK

Description of Material	Nitrogen	Carbon and Org. Mat.	Phosphate of Lime	Carbonate of Lime	Other Con- stituents
	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
Charcoal, fine, new ...	1.12	11.6	73.1	8.0	7.3
“ once used ...	1.95	21.1	64.6	6.4	7.9
“ fine, new	1.22	11.3	72.2	5.3	10.5
“ once used ...	2.83	32.0	53.7	4.9	9.4
“ twice used ...	3.59	42.2	46.0	3.3	8.5
“ fine, new	1.61	11.0	75.6	7.0	13.4
“ once used ...	2.54	36.2	52.6	10.0	10.1
“ twice used ...	3.18	42.5	47.5	4.5	5.2

Bone ash is merely the mineral matter which remains after bones have been burned for fuel. At one time large quantities of this ash were shipped to the United States and Europe from certain South American countries. The immense prairies in Argentine for instance support vast herds of cattle and a century or more ago these animals were often slaughtered merely for their skins, horns and fat. According to Fritsch the flesh was seldom used for human food and the bones were consumed for domestic fuel. Thus great mounds of bone ash accumulated the value of which was not appreciated until many years later. When the importance of this high grade phosphate was recognized, however, the bone ash was hauled to the seaboard and shipped to foreign countries where it was used for manufacturing very high grade acid phosphate and pure phosphate products.

This material is now nearly exhausted and the ancient practice of burning bones and thus destroying much of their commercial value is generally recognized as a profligate waste. Bone ash, however, is a very high grade raw phosphate material and finds a ready market where relatively concentrated or pure phosphate products are manufactured. The following analyses of typical samples of bone ash show how free most of this material is from objectionable impurities.

TABLE V
CHEMICAL COMPOSITION OF FIVE TYPICAL SAMPLES OF BONE ASH

Sample No.	1	2	3	4	5
	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
Moisture and organic matter	8.89	19.66	17.37	3.39	10.30
P ₂ O ₅	35.38	33.89	32.63	38.12	29.56
CaO	47.80	43.00	39.76	48.92	35.50
MgO	0.97	0.97	1.48	5.67	4.40
Na ₂ O, K ₂ O	1.39	0.84		
Fe ₂ O ₃	3.01	0.78	0.21		
CO ₂			0.84	3.90	20.24
SiO ₂	6.95	8.31	6.50		

Guano.—The word guano is derived from the Peruvian word huanu meaning excrement. This material is the oldest fertilizer known to man, for the literature shows that the excrements of birds and animals were used for agricultural purposes at least 200 years B. C. While there appears to have been a period during which the fertilizer merits of guano were unappreciated or forgotten in certain European countries, it again came into use in 1840 ⁴⁸ when a firm of Lima merchants sent a cargo of Peruvian guano to London. Twenty-two years later (1862) the annual exports of guano from Peru had risen to 435,000 tons.

Although guano occurs in natural deposits it can not on the whole be properly classed among the relatively insoluble phosphates since its composition and agricultural availability varies between wide limits depending upon the source of the materials, the conditions under which it has been laid down and the natural agencies to which it has been exposed.⁴⁹

The guano deposits found in arid regions or in caves (bat guano) where the material has not been subjected to the leaching action of water contain, as a rule, their phosphoric acid in a much more soluble and available form than the guano which has been leached by percolating waters. The former material also contains, in addition to the phosphoric acid, considerable amounts of nitrogen, which increases greatly its commercial value. Between the two extremes of guano containing nearly all of its original organic matter and that which has been so weathered as to resemble phosphate rock there are many deposits in various stages of decomposition. Most of the guano entering the fertilizer market comes from India, Africa, the West Indies, Argentine, and certain islands off the Coast of Peru and is chiefly derived from either the accumulation in caves where great numbers of bats congregate or from the droppings of birds which feed upon fish and marine animals. Because of the great variation in the composition of guano it is seldom purchased without the buyer knowing definitely the percentages of nitrogen and phosphoric acid (both available and insoluble) which it contains.

The most famous deposits of guano are those occurring on certain groups of islands off the coast of Peru ⁵⁰ where for thousands of years vast numbers of fish eating birds have nested and reared their young. The dung and remains of countless generations of these marine birds

⁴⁸ Peruvian Guano Deposits, Am. Fert. Handbook, pp. 30-34 (1910).

⁴⁹ Fritsch, Mfg. of Chem. Manures, pp. 50-59 (1911); Gile and Carrero, Bat Guanos of Porto Rico, Bull. 25, Porto Rico Exper. Sta. (1918).

⁵⁰ Peruvian Guano Deposits, Amer. Fertilizer Handbook, p. 30 (1910); Peru's Wealth in Guano, Pan American Magazine, Vol. 16, No. 5, p. 50 (1913); West Coast Leader, p. 15, Aug. 18 (1913).

have accumulated in guano beds which have reached a thickness in certain places of over 100 feet.

These deposits probably represent the most valuable natural fertilizer known to the world since they occur in a rainless region and hence have retained nearly all of their soluble constituents. It is true that large guano deposits derived from the same source (the dung of marine birds) are found upon islands in the Caribbean Sea, upon the coast of Africa, and on other islands of the Pacific Ocean but practically all of these deposits occur in humid regions where the rainfall has leached away much of their content of nitrogen leaving a residue of the less soluble phosphates.

The nitrogen content of Peruvian guano, however, seldom falls below $8\frac{1}{2}$ per cent and will often run as high as 16 per cent. This material, therefore, is valued chiefly as a nitrogenous fertilizer although it contains a high percentage of phosphoric acid (much of which is citrate soluble) and appreciable quantities of potash.

At one time these guano deposits constituted an important source of revenue to the Peruvian government, but for years their exploitation was carried on so indiscriminately and with so little regard for the future that they have been very much depleted and it finally became evident that they would soon be exhausted unless steps were taken to conserve them and protection afforded the birds from which they are derived. According to Coker⁵¹ more than 10,000,000 tons of Peruvian guano valued at from \$400,000,000 to \$600,000,000 were extracted and shipped from one small group of islands between 1851 and 1872.

About this time, however, laws were passed limiting the exports of guano, and later, regulations were adopted whereby the islands were mined in rotation and the extraction of guano restricted so as to interfere as little as possible with the birds, particularly while they are breeding. In this way the supplies of guano are being to a certain extent replenished but at a rate hardly more than sufficient to meet the demands of domestic agriculture. Coker⁵² found that in certain rookeries where the birds were left unmolested the guano accumulated at the rate of $4\frac{1}{2}$ inches per annum or 300 pounds to the square yard. This annual deposition seems almost incredible until one considers that some of these marine birds consume as much as 8 to 10 pounds of fish each day and their nests are frequently built so close together as to resemble eggs in a crate.

Bat guano is another type of natural nitrogenous phosphate fertilizer but it does not on the whole compare in value to Peruvian guano. The deposits are much smaller, the annual accumulations far less (due

⁵¹ Peru's Wealth Producing Birds, Nat. Geog. Mag., Vol. 37, p. 537 (1920).

⁵² Idem.

to the relatively small quantities of food consumed by bats) and the caves in which the material is deposited are frequently so isolated that it hardly pays to exploit them. Moreover, the composition of bat guano varies greatly not only in different caves but in different parts and at various depths of the same cave depending upon the amount of percolating water entering the cave, the intrusion of soil or other foreign material, the type of the rock forming the base of the cave and the character of the bacterial activities which function under different conditions. Gile and Carrero⁵³ made a very complete examination of a large number of samples of bat guano from various parts of Porto Rico and found that the nitrogen content of this material ranged all the way from an almost negligible amount to 13.04 per cent and the phosphoric acid from less than 1 per cent to 41.58 per cent.

Most of the guano, even that which has been largely leached of its more soluble constituents is ground and applied directly upon the field, although some is treated with sulfuric acid and its fertilizer constituents thereby rendered more soluble and quickly available to crops.

Apatite.—Apatite is a phosphate mineral having a regular crystalline structure (hexagonal) and a more or less definite chemical composition. Two varieties of this mineral are recognized, namely, chlorapatite $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ and fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$.⁵⁴ These two types contain when pure from 40.9 to 42.26 per cent of P_2O_5 which is a higher phosphoric acid content than any other phosphate mineral found in large deposits.

While widely distributed in nature apatite occurs chiefly as veins or intrusions in igneous rocks and therefore is probably derived directly from the molten magma. It has been prepared synthetically in the laboratory by a number of investigators both from mixtures of highly heated or fused materials⁵⁵ and by heating said mixtures with water under pressure.⁵⁶

It is generally conceded that apatite is the original source of practically all natural commercial phosphates. Since it is appreciably soluble in carbonated waters some of the mineral is constantly being carried to the sea where it is absorbed and concentrated by living organisms, some portions react with other products of rock decomposition forming new secondary phosphates which may be subsequently segregated in

⁵³ Bat Guanos of Porto Rico, Bull. 25, Porto Rico Experiment Station (1918).

⁵⁴ Voelcker, Ber. Deutsch. Chem. Gesell., Vol. 16, p. 2460 (1883); Dana, System of Mineralogy, pp. 530-531; Clarke, Data of Geochemistry, 2d Edition, Bull. 491, p. 336, U. S. Geol. Survey (1911).

⁵⁵ Daubree, Compt. Rend., Vol. 32, p. 625 (1851); Manross, Liebigs Annalen, Vol. 82, p. 353 (1852); Porchammer, Liebigs Annalen, Vol. 90, pp. 77 and 332 (1854); Deville and Caron, Compt. Rend., Vol. 47, p. 985 (1858).

⁵⁶ Debray, Compt. Rend., Vol. 52, p. 44 (1861).

relatively large deposits, other portions enter the soil and are taken up by plants which in turn may be either consumed by men and animals and the phosphoric acid thus utilized to build up bone and tissue, or the phosphate may be again returned to the soil in altered form after the death and decay of vegetable life.

Although sometimes found in large bodies, apatite like nearly all mineral veins or intrusions is very irregular in occurrence.

The most important deposits are found in Norway, Spain and Canada and before the discovery of the immense deposits of amorphous phosphates in the United States the mining of Canadian apatite was conducted on a fairly extensive scale.⁵⁷ The peak of production in Canada was reached, however, in 1890 when the annual output amounted to 31,753 tons. Since that date the industry has steadily declined and as early as 1896 the annual production had fallen to 570 tons.

Large reserves of apatite still remain in the provinces of Ontario and Quebec⁵⁸ but the small tonnage which enters the market is obtained merely as a by-product in the mining of mica with which the apatite of the latter province is associated. The irregularity and uncertainty of vein deposits and the hardness of the country rock make the cost of prospecting and mining apatite relatively high. Moreover, the material must be cobbled or hand picked in order to insure a high grade product which adds further to the final cost. It is a significant fact that the three countries mentioned above have not only ceased to export apatite but practically all of the phosphatic fertilizer manufactured for domestic use is produced from amorphous phosphate rock imported from Africa or the United States.

Phosphorite or Phosphate Rock.

Phosphorite or amorphous phosphate rock which occurs in sedimentary deposits (usually of marine origin) in many parts of the world is by far the most important of the raw materials used as sources of phosphoric acid for fertilizer and other industrial purposes.

Few minerals marketed today are found at a greater number of geologic horizons and occur under a wider range of natural conditions than phosphate rock. It is found in deposits of Ordovician, Silurian, Devonian and Carboniferous Age, in Jurassic, Cretaceous, Tertiary and even more recent strata. In physical properties it varies all the way from hard flintlike masses to soft plastic material resembling kaolin,

⁵⁷ Wyatt, *Phosphates of America*, pp. 27-44 (1892).

⁵⁸ The Mineral Indust. of the British Empire, Imp. Mineral Resources Bureau, pp. 35-37 (1921); Spense, *Phosphate in Canada*, Report of the Canadian Dept. of Mines (1921).

and from black massive seams of rock which have been mistaken for coal to brown, porous thin bedded strata or to small white nodules and pebbles. There are deposits which show little evidence of organic origin and others which are largely made up of fossilized bone, teeth and the waterworn casts of phosphatic shells.

While different deposits as well as the several strata in the same deposit may vary considerably in value and extent, phosphate rock on the whole is readily and cheaply mined, and there is little doubt that the abundance and low cost of this mineral are largely responsible for the expansion of the fertilizer industry and the economic maintenance and increase in crop yields.

The ratio of lime to phosphoric acid in the purest samples of phosphorite approaches that in fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) or tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$),⁵⁹ but nearly all phosphate rock contains as impurities various amounts of organic matter, iron and aluminum oxides or phosphates, carbonates of lime and magnesium and calcium fluoride. Moreover, nodular and plate phosphates are usually found mixed with clay and sand from which they must be separated by a washing process, or in the case of the bedded deposits the rock may be interstratified with limestone and shales entailing selective mining in order to obtain a marketable product.

The phosphate rock deposits of the world in the order of their present commercial importance are as follows:

The phosphates of the United States including those of great value and extent in Florida, Tennessee and the western states, Utah, Idaho, Wyoming and Montana and deposits of less importance in South Carolina, Kentucky and Arkansas; the deposits of northern Africa in Algeria, Tunis, Egypt and Morocco; the deposits in the Pacific and Indian Oceans including those of Ocean, Christmas and Nauru Islands, and islands of the Marshall, Pellew and Society groups; deposits of less importance in Australia, Japan and New Zealand; the phosphates of Russia, Belgium, France, England; and a number of smaller deposits in various other countries. The world's output of phosphate rock based on material marketed for eight years is given in detail in Table VI.

• Finely Ground Raw Rock Phosphate.

In order to maintain indefinitely the fertility of soils with respect to phosphoric acid, a number of agronomists and agricultural chemists recommend the application of finely ground unacidulated raw rock phosphate directly on the field. A considerable tonnage is thus annually

⁵⁹ Clarke, F. W., *Date of Geochemistry* (2nd Edition), Bull. 491, U. S. Geol. Survey, p. 499 (1911).

TABLE VI

PRODUCTION OF PHOSPHATE IN THE WORLD^a

(In metric tons)

	1917	1918	1919	1920	1921	1922	1923	1924
Algeria	*202,539	*198,539	271,162	502,931	402,884	489,277	464,064	583,234
Angaur Island	^c	30,000	30,000	^b 30,000	^b 30,000	^b 30,000	^b 30,000
Australia	8,626	11,918	9,151	13,339	7,101	3,956	1,000
Belgium	138,800	61,700	90,970	133,040	55,040	56,840	55,584	^b 50,000
Canada	135	127	24	Nil	27	172	27	Nil
Christmas Island	89,889	53,378	69,719	70,690	*87,898	*100,952	*71,567	^b 90,000
Dutch W. Indies (Aruba & Curacao)	3,639	9,890	61,486	60,858	56,065	85,855	^b 75,000
Egypt	115,732	31,147	29,365	114,813	122,024	60,220	25,370	^b 50,000
France	^c	103,869	124,930	113,800	99,600	78,000	2,250
Japan	121,609	191,722	122,868	97,340	31,994	12,327	33,099	^b 10,000
Madagascar	*5,210	Nil	*743
Makatea Island	32,259	^b 40,000	^b 40,000	*30,000	59,552	77,482	82,866	^b 75,000
Morocco	6,981	96,317	225,395	436,000
New Zealand	5,050	5,000	4,064	5,427	6,109	3,178	2,421	^b 3,000
Nauru Island	98,000	83,000	60,000	100,000	^b 100,000	*367,001	*185,103	^b 275,000
Norway	1,832	4,562	1,168
Ocean Island	200,000	^b 200,000	^b 200,000	^b 200,000
Russia	375	9,800	^b 10,000	^b 10,000	^b 10,000
Spain	28,148	43,303	25,035	42,896	38,055	6,491	5,397	5,000
Tunis	999,326	818,962	815,385	1,075,180	1,828,000	2,115,000	2,357,000	2,871,600
United States	2,652,776	2,530,861	2,465,203	4,170,056	2,097,256	2,471,036	3,055,114	2,913,960
Total	4,498,360	4,074,211	4,147,873	6,678,612	5,257,379	421,190 ⁹	6,967,862	7,680,787

^a Based on marketed output. ^b Estimated.
figures for Nauru Island. ^c First 6 months.^{*} Statistics not available. ⁹ Includes Ocean Island. ^{*} Exports. ^{*} Included in

employed chiefly in the state of Illinois where the late Dr. Cyril G. Hopkins consistently advised its use in connection with crop residues, manure or other forms of organic matter. From a strictly theoretical standpoint it would appear that finely ground raw rock phosphate should be an effective phosphate carrier, particularly when applied to soils low in phosphoric acid. Certainly we know that the mineral phosphates of the soil which normally support plant life have no greater solubility than phosphate rock. In fact iron and aluminum phosphates which are probably the chief compounds of phosphoric acid in most soils are considerably less soluble than tricalcium phosphate, the main compound present in phosphate rock. This latter compound is known to be appreciably dissolved by carbonated waters and therefore it should enter the soil solution which is nearly always rich in carbon dioxide.

The agricultural value of finely ground unacidulated mineral phosphates does not lack practical supporting evidence. Many experiments conducted in the laboratory greenhouse and field point strongly to the merit of this material and the author, in a compilation and classification⁶⁰ of all the long time experiments conducted with raw rock phosphate, found that as far as the data would admit of conclusions this material usually gave increased crop yields and from a financial standpoint the results obtained often compared favorably with those from other types of phosphatic fertilizers. Very fine grinding, liberal applications, and the presence in the soil of fairly large amounts of organic matter are important factors, however, in determining the effectiveness of raw ground phosphate rock as a fertilizer and even when all the conditions are favorable to its ready utilization it should not be expected to give as quick returns as the more soluble phosphatic fertilizers.

⁶⁰ Waggaman and Wagner, Bull. 699, Department of Agriculture (1918).

Chapter 2.

Phosphates of the United States.

Florida.

The most extensively exploited deposits of phosphate in the world are those of Florida and since 1888 when the first 3,000 tons were shipped from the Peace River District the production of Florida phosphate has steadily increased with the exception of a few years when adverse conditions temporarily reduced the output.

So many excellent papers¹ have been published discussing the his-

¹For the history, geology, and descriptions of the Florida Phosphate deposits see Hawes, Geo. W., A Phosphatic Sandstone from Hawthorne, Florida Nat. Museum proceedings, pp. 46-48 (1883); Mineral Resources, U. S. Geol. Survey, 1883 to 1921, inclusive; Smith, E. A., Phosphatic Rocks of Florida, Science 5, pp. 395-396 (1885); Penrose, R. A. F., Jr., Nature and Origin of Deposits of Phosphate of Lime, Bull. 46, U. S. Geol. Survey (1888); Ledoux, A. R., The Newly Discovered Phosphate Beds of Florida, N. Y. Acad. Science, Trans., 9, pp. 84-94 (1890); Pickel, J. M., Florida Phosphate, Fla. Agr. Exp. Sta. Bull. 10, pp. 6-11 (1890); Cox, E. T., An Extensive Deposit of Phosphate in Florida; Wyatt, Francis, Phosphates of America (187 pages) (1891); Darton, N. H., Notes on the Geology of the Fla. Phosphate Deposits, Amer. Jour. Sci., 41, pp. 102-105 (1891); Millar, C. C. H., Florida, S. Carolina and Canadian Phosphates, 223 pages (1892); Dall, W. H., and Harris, G. D., Correlation Papers, Neocene of North America, U. S. Geol. Survey, Bull. 84 (1892); Eldridge, G. H., A Preliminary Sketch of the Phosphates of Florida, Amer. Inst. Min. Eng. Trans., 21, pp. 196-231 (1893); Wright, Carroll D., The Phosphate Industry of the United States, 6th Special Report of Commissioner of Labor, Wash., D. C., pp. 23-69 (1893); Cox, E. T., Geol. Sketch of Florida, Amer. Inst. Min. Eng. Trans., 25, pp. 28-36 (1896); Wells, G. M., The Fla. Rock Phosphate Deposits, Amer. Inst. Min. Eng. Trans., 25, pp. 163-172 (1896); Codington, E. W., The Florida Pebble Phosphates, Amer. Inst. Min. Eng. Trans., 25, pp. 423-431 (1896); Brown, L. P., Phosphate Deposits of the Southern States, Eng. Assoc. of the South Proc., 15, No. 2, pp. 63-86 (1904); Jumeau, L. P., Le Phosphate de Chaux et les Exploitations aux États-Unis, Paris, 198 pages (1905); Matson, C. G., and Clapp, F. G., A Preliminary Report on the Geology of Florida, Fla. State Geol. Survey, 2nd Ann. Report, pp. 21-173 (1909); Sellards, E. H., A Preliminary Paper on the Fla. Phosphate Deposits, Fla. State Geol. Survey, 3d Annual Report, pp. 17-41 (1910); Waggaman, W. H., A Review of the Phosphate Fields of Florida, Bull. 76, Bureau of Soils (1911); Brown, L. P., The Phosphate Deposits of Continental North America, 8th Int. Congress of Applied Chemistry, 26, pp. 87-113 (1912); Sellards, E. H., Origin of the Hard Rock Phosphates of Florida, 5th Annual Report, Fla. Geol. Survey, pp. 27-80 (1913); Sellards, E. H., The Pebble Phosphates of Florida, 7th Annual Report, Fla. Geol. Survey, pp. 29-116 (1915); Matson, G. C., The Phosphate Deposits of Florida, Bull. 604, U. S. Geol. Survey (1915); Mansfield, G. R., Phosphate Resources of the U. S., pp. 8-15 (1917); Dobbins, W. J., Mining and Washing Phosphate Rock in Florida, Eng. & Min. Jour Press, Vol. 116, p. 577 (1923).

tory geologic occurrence and origin of these deposits and describing the physical and chemical properties of the several types of rock and the methods of mining, washing, drying and marketing the product, that the writer hardly feels justified in giving more than brief descriptions of these deposits.

There are three classes of phosphate mined in Florida, namely, the hard rock, the land pebble, and soft phosphate. The last mentioned, however, has at present but little commercial significance since it is expensive to separate in a pure state and is not generally considered desirable for the manufacture of soluble phosphatic fertilizers and pure phosphate products. The river pebble phosphates formerly dredged from the beds of streams belongs to a more recent geologic period than the hard rock, or land pebble types and is still accumulating in certain rivers which drain the phosphate area. These deposits owe their immediate origin to the formation across which the stream flows. The river pebble, however, is as a rule of somewhat lower grade than the land pebble phosphate and its recovery is more costly. The exploitation of these deposits, therefore, gradually fell off and in (1908) ceased entirely.

The hard rock phosphate region lies towards the west side of the Florida Peninsula, extending in a north and south direction from Suwannee and Columbia Counties to Citrus and Hernando Counties, a distance of over 100 miles. Excellent transportation facilities are furnished by two railroads and most of the material is transported to ports on both sides of the peninsula and from there shipped chiefly to foreign countries.

The hard rock phosphate belongs to the Tertiary or Oligocene epoch. The rock occurs as nodules and boulders in irregular pockets which vary in size from a few square yards to several acres in extent, these nodules being imbedded in a matrix of sand, clay and soft phosphate. The deposits which are covered by an overburden of sand and clay varying from a few inches to 30 feet or more in thickness usually rest upon a thick and relatively pure light colored cavernous limestone known locally as the Vicksburg formation.²

Numerous theories have been advanced to explain the origin and formation of these deposits and since the remains of terrestrial and marine life are found closely associated with the phosphate the earlier geologists favored the theory that they are largely derived from organic sources. Dall ³ and Millar ⁴ were of the opinion that guano was prob-

² Sellards, E. H., Origin of the Hard Rock Phosphate Deposits of Florida, 5th Annual Report Florida State Geol. Survey (1913); Matson, G. C., The Phosphate Deposits of Florida, Bull. 604, U. S. Geol. Survey (1915).

³ Bull. 84, U. S. Geol. Survey, pp. 134-140 (1891).

⁴ Florida, South Carolina and Canadian Phosphate, pp. 116-118 (1892).

ably the original source of these phosphate deposits. The former believed that the phosphoric acid was leached out of such material as fast as it was formed and taken up or fixed by the underlying limestone. He thought it doubtful, however, that the frequent occurrence of bones and teeth has any bearing on the origin of the phosphate beds since such remains occur in many localities where the phosphate deposits are lacking. Pratt ⁶ believed that the phosphate boulders are the fragments of the fossil remains of gigantic foraminifera which either perished through natural causes or were preyed upon by higher forms of marine life. Eldridge ⁷ divides the hard rock deposits into three periods, first that in which the primary rock was formed from underlying limestones through the displacement of carbonic acid by phosphoric acid; second, that of secondary deposition in the cavities of the primary rock; and third, that in which the deposits thus formed were broken up and mixed with foreign material. Jumeau ⁸ attributes the formation of the Florida phosphates to the secretion and subsequent deposition of phosphate of lime by lower marine forms; to the excreta of birds which feed on marine life; and to the deposition of bones of innumerable animals driven south by the intense cold of the glacial period. Brown ⁹ and Matson ¹⁰ are inclined to the theory that the phosphoric acid from which the Florida phosphates are derived was originally disseminated through the Vicksburg limestone in the form of nodules and in shells of phosphate secreting animals. Some of the phosphoric acid was concentrated by solution and redeposition, replacing the carbonic acid of the limestone. Subsequent disintegration of the rock freed these nodules from the surrounding limestone and they were finally concentrated in sinks by streams or ocean currents, or by both. Matson ¹⁰ states that with few exceptions the deposits are all of secondary origin. Sellards ¹¹ believes that the hard rock deposits are derived from formations of upper Oligocene Age which are now almost entirely lacking in the phosphate area, but which are found bordering these regions. He considers the hard rock deposits made up largely of the residue of these formations which have disintegrated in place. He considers that the replacement of the original limestone by calcium phosphate was an important factor in the formation of these deposits, also that the precipitation of

⁶ An official report made on 8,000 acres of phosphate property in Fla. (1890).

⁷ Trans. Am. Inst. Min. Eng., Vol. 21, pp. 196-251 (1891).

⁸ Le Phosphate de Chaux et Les Exploitations Aux États-Unis, Paris (1905).

⁹ Phosphate Deposits of the Southern States; Engineering Asso. of the South, trans., Vol. 15, No. 8, pp. 63-66 (1904).

¹⁰ The Phosphate Deposits of Florida, Bull. 604, U. S. Geol. Survey, p. 54 (1915).

¹¹ Bull. 604, U. S. Geol. Survey, p. 45 (1915).

¹² Origin of the Hard Rock Phosphate Deposits of Fla. 5th ann. report, Fla. State Geol. Survey, pp. 23-30 (1913).

phosphoric acid from solution contributed further to the enrichment of these deposits.

While the hard rock phosphate varies considerably in its physical properties, on the whole it consists of hard white or cream colored nodules or boulders, sometimes having cavities filled with foreign material derived from the matrix of sand and clay and soft phosphate in which the material is imbedded. The phosphate beds vary greatly in thickness (even within a very small area) ranging all the way from a few feet to 70 feet or more. The percentage of recoverable rock in the matrix also differs widely from place to place. The average grade of the rock after washing and drying is 77 per cent tricalcium phosphate (bone phosphate of lime) and less than three per cent of iron and aluminum oxides.

The following description is given by Mansfield¹² on the method employed in prospecting for hard rock phosphate.

"In the hard-rock field of Florida the bedrock is so rough and the distribution of the phosphate-bearing matrix so irregular that detailed prospecting must be done before any commercial exploitation may be attempted. In usual practice holes are spaced not more than 50 feet apart, and where greater detail is needed the distance between holes is reduced to 25 feet or less. In preliminary work holes may be spaced at 100 to 200 foot intervals; then intermediate holes are placed as necessary. In this way the shape and size of a commercial body of ore are carefully outlined. In 50-foot spacing a 40-acre tract systematically tested would contain 26 lines of holes with 26 holes each, a total of 676 holes, or about 17 holes to the acre.

The overburden is usually removed by "cupping." The "cup" is a vertically slit iron cylinder about 1 foot long and 2 inches in diameter attached to drill rods or pipe, which may be used in 5-foot or other convenient lengths. When the phosphate is reached or the overburden is too tough or hard for the "cup" the hole is cased with 2-inch double-thick pipe, and a chisel bit with ball valve, mounted on a 1 $\frac{7}{8}$ -inch pipe, is introduced. Drilling may be done either by man power, with a simple tripod and pulley, or by a power drill. The thickness of the phosphate matrix is determined together with the amount and quality of the washed and dried phosphate rock. On this basis the tonnage is computed for the area examined.

According to experienced operators a hard-rock plant would ordinarily cost about \$100,000, and the minimum quantity of rock in sight for such a plant should be 50,000 tons, though a favorably located and shaped body of ore containing as little as 15,000 tons might be worked with a smaller plant. A small body of ore adjacent to an operating

¹² Phosphate Rock, Mineral Resources, Part II, U. S. Geol. Survey (1923).

plant might be worked at profit, whereas by itself it would not be profitable.

In prospecting of this sort much barren ground must be tested in the course of locating and testing a commercially valuable body of rock. The cost of such work averages \$300 or more to the acre.

Florida hard rock phosphate is mined by first removing the overburden of sand and clay and then digging out or dredging the phosphate stratum thus exposed. The thickness and character of the overburden varies considerably and upon this depends largely the cost of production. The depth of the overburden is not now considered as important as it was during the early development of these deposits, whereas 10 to 15 feet of overburden was at once considered too great to be economically removed, prospecting is now carried to a depth of 50 feet. The overburden is removed by scrapers, steam shovels or by hydraulic means. The type of mining employed (dry or dredge mining) depends on whether or not the deposit occurs above or below the normal water table. In the dry mines the phosphate bearing material may be removed either by hand labor (pick and shovel) or by mechanical means (steam shovel). Blasting is often resorted to to break up the large boulders of phosphate. In the mines where the phosphate deposits lie below the water level, large dredges are floated in the beds and phosphate and matrix scooped up and loaded into cars for shipment to the washer plant. The latter method does not permit of selective mining and the outlay of capital for machinery is usually somewhat greater.

The phosphatic material is brought from the mines in tram cars, hauled up an inclined track to the washer plant and dumped upon a grizzly or grating having bars about 2 to 2½ inches apart which allow the smaller fragments of rock and matrix to pass through into the washer. Large boulders are broken up, thrown back upon the grizzly and hence also pass to the washer.

The washer consists of one or more pair of wooden logs, 30 feet in length and 18 inches in diameter which revolve in opposite directions in an inclined trough. A series of blades or teeth bolted to the logs in spiral form work up the phosphate and matrix as it enters the lower end of the trough and carry the material forward with constant rubbing, while streams of water are continuously sprayed upon it. The adhering sand, clay and soft phosphate are thus separated from the rock, and the water carrying these impurities in suspension flows back towards the lower end of the trough and is discharged into a flume which carries it to waste ponds situated some distance from the plant. From the logs the rock passes into one or more revolving rinsers which consist of double shell cylinders made of perforated steel plate, the inner shell has perforations 1½ inch \times ¾ inch and the outer shell per-

forations $\frac{1}{8}$ inch \times $\frac{1}{16}$ inch. In the rinsers the material is sprayed with further quantities of water and the remaining particles of adhering clay loosened and washed away. A separation of coarse and fine phosphate rock is also effected at this point—the larger lumps retained by the coarse mesh of the inner cylinder are discharged upon a picking table or belt where flint, limestone fragments and clay balls are removed. The finer particles which pass through the inner screen but are retained by the outer screen are discharged into a pit, taken up by elevators and

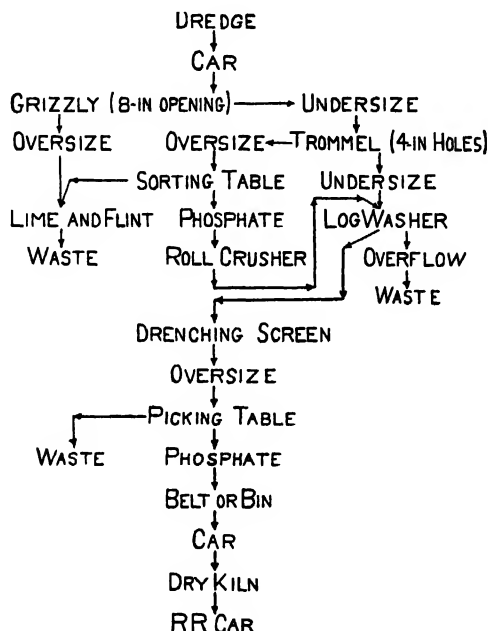


FIG. 1 Flow Sheet of Typical Phosphate Washer in Hard Rock District.

dumped into bins or upon piles to drain. The washed rock is then dried either by burning on ricks of wood or in rotary kilns somewhat similar to those employed in the cement industry. While the former method is still used to some extent in the hard rock phosphate area, it is gradually being replaced by the latter method where crude oil is used as a fuel and the drying process completed more quickly. The flow sheet of a typical phosphate washer in the hard rock area is shown in Figure 1.

In order to meet the demand for a high grade product a large amount of phosphate material is annually lost in the washing process. The marketed product is seldom more than 10 per cent of the total material mined and usually less. The remaining 85 per cent consisting of sand,

clay, soft phosphate and fine particles of relatively high grade rock is discharged into the waste pond. This discarded material varies in its content of phosphoric acid, but will contain on the average at least 10 per cent of P_2O_5 . The amount of phosphoric acid thus discarded, therefore, is greater than that actually saved and while this waste covers large areas in the vicinity of old phosphate plants no method has yet been devised whereby its phosphoric acid content can be economically extracted.

Mining operations in the hard rock fields have fallen off somewhat in recent years since the cost of producing this high grade material is far greater than that of mining the more regular deposits of pebble phosphate occurring further south in this state. Moreover, the demand for this rock in certain foreign countries which formerly purchased most of the output has decreased considerably due to the unfavorable rate of exchange and to the increased development of the deposits of phosphate rock in northern Africa. While many of the hard rock deposits have been worked out there still remains a large tonnage of this exceptionally high grade material and it is probable that this field will continue to be a factor for many years to come.

It is rather difficult to arrive at the present average cost of producing Florida hard rock phosphate for the market, not only because of the irregular occurrence of the deposits and the wide fluctuations in the quantity of rock recovered per ton of material handled, but also on account of the unsettled industrial conditions which have prevailed ever since the war. These conditions continue to affect the price of labor, fuel and mechanical equipment.

The figures given in Table VII are compiled from data obtained from a number of operators in these fields and though somewhat approximate may be regarded on the whole as fairly conservative.

TABLE VII
AVERAGE COST (PER LONG TON) OF PRODUCING FLORIDA HARD ROCK PHOSPHATE
FOR THE MARKET

Items	Cost per Long Ton
	Dollars
Labor *	1.75
Drying rock (fuel)30
Depreciation on land25
Depreciation on plant50
Power (electric or steam)50
Maintenance35
Taxes and insurance10
Interest at 6 per cent15
Total cost †	3.90

* Includes labor for mining, washing, drying and storing.

† Exclusive of overhead charges.

The pebble phosphates of Florida are the most extensively worked of any in the world. The phosphate area at present productive includes the eastern part of Hillsboro, the southwestern part of Polk and the northwestern part of Desota Counties. The chief mines being in Polk and Hillsboro Counties some 20 to 40 miles east of Tampa to which port the bulk of the phosphate is shipped. Three railroads serve the pebble phosphate regions.

These deposits are also of Tertiary Age, but are more recent (Pliocene) than the hard rock phosphate. The chief formation in which they are found is commonly known as the "Bone Valley Gravel."

Darton¹³ considered that these deposits are derived from the hard rock phosphate, since the pebbles are similar in appearance and overlap those older beds as a shore deposit. Eldridge¹⁴ while inclined to the view that the pebble deposits are probably composed of the rolled fragments of preëxisting beds doubted that they were derived from the hard rock phosphate. In discussing the origin of the land pebble phosphate Eldridge quotes from an unpublished paper of Shaler, in which the author attributes the formation of phosphate pebbles to the leaching action of phosphate solutions upon soft, porous marls, the replacement of carbonic by phosphoric acid being accompanied by a certain degree of disintegration. The fragments thus formed when subjected to some concretionary deposition and attrition assumed a pebble form. This author further states that it is evident the pebble deposits have been subjected to erosive forces, since the beds in the valleys are much thicker than those in the uplands.¹⁵ The frequent occurrence of sharks' teeth and other marine remains indicate that this erosion was caused by the action of the sea. Sellards¹⁶ considers that these deposits are also derived from the same source as the hard rock phosphate but that the processes by which they have accumulated in their present form are strikingly different. He believes the hard rock phosphate deposits are chemical precipitates or replacement deposits, but that the land pebble phosphates are residual deposits from erosion of the parent formation. Moreover, where the hard rock phosphates occur in sections where the parent formation has entirely disintegrated over limestones, the land pebble phosphates are formed as a blanket deposit resting upon and representing a concentration from the parent formation. In a somewhat more recent investigation Matson¹⁷ found that while the Bone Valley

¹³ Amer. Jour. Science, 3d series, Vol. 41, p. 105 (1891).

¹⁴ Amer. Inst. Min. Eng. Trans., Vol. 21, pp. 218-219 (1893).

¹⁵ Extensive developments in the pebble fields, however, have shown that many of the best beds of phosphate are found in the uplands.

¹⁶ The Pebble Phosphates of Florida, 7th Ann. Report of the Florida Geol. Survey (1915).

¹⁷ The Phosphate Deposits of Florida, Bull. 604, U. S. Geol. Survey, p. 35 (1915).

formation is the chief source of the pebble phosphate there are a few mines which obtain some phosphate from strata lying unconformably below this formation. This discovery may have an important commercial significance in future prospecting and exploitation work.

The pebble phosphate region is relatively level and the deposits on the whole far more regular in their occurrence than those in the hard rock regions. While the pebbles are imbedded in a matrix of sand and clay somewhat similar to that in which the hard rock is found, the yield of product per ton of material handled is on the average considerably greater than the yield of hard rock phosphate.

Mansfield¹⁸ gives the following brief description of the method employed in prospecting for Florida pebble phosphate, the value set on the rock in the ground, and the cost of the average phosphate plant.

"In the pebble field the phosphate matrix, though variable in quality and thickness, is much more regular than that of the hard-rock field, and fewer holes are needed. In commercial practice 16 holes are ordinarily sufficient to test a 40-acre tract. The method of prospecting is slightly different from that used in the hard-rock field. The whole operation is done with a modified form of posthole auger 4 inches in diameter, and 4½ inch casing is sunk at the same pace as the auger. The phosphate matrix removed from the auger is weighed after the water has been allowed to drain away, then washed over a standard screen, and the phosphate is dried over a fire and weighed. From the thickness of the matrix, the weight of the phosphate rock recovered, and the percentage of phosphate to matrix the tonnage of phosphate rock in the tract is computed according to a formula such as the following, which is used by one of the larger companies: Area (square feet) × thickness of matrix (feet) × weight per cubic foot (pounds) × percentage of rock in matrix ÷ 2,240. The grade of the available rock is determined by analysis. A sample prospecting summary for a 40-acre tract shows the total area, the minable area, the total minable tonnage and the average per acre, the average tricalcium phosphate, the average iron and alumina, and the average overburden per acre and per ton. The cost of such prospecting work was stated by one company to have averaged \$8.00 an acre for a tract of 2,000 acres.

Pebble-phosphate plants operate on a larger scale than hard-rock plants and require a far larger tonnage of minable rock. For example, a plant with an annual capacity of 100,000 tons a year is said to cost about \$500,000 to build. Depreciation, as in the hard-rock field, is heavy. For such a plant probably as much as 4,000,000 tons of rock should be in sight.

In pebble fields the depth of the overburden is of much less conse-

¹⁸ Mineral Resources, Part 2, p. 255, U. S. Geol. Survey (1923).

quence in mining operations than formerly, though it must always impose limits upon exploitation. Whereas 10 to 15 feet of overburden was once considered excessive, and later intermediate limits were set, prospecting is now continued to a depth of 55 or 60 feet.

In the pebble field, land is sold at a price per ton of rock in the ground. In May, 1923, the writer was informed that land containing 2,000 tons of phosphate to the acre would be considered minable under favorable conditions. An average overburden of 7 to 8 cubic yards to the ton of rock for the whole area would be the limit for ordinary-grade rock. One tract was sold in which the overburden averaged $8\frac{1}{2}$ cubic yards, and for another in which the rock was of high grade 10 cubic yards was the limit set. The price per ton of rock in the ground was said to have ranged from $3\frac{1}{2}$ to 15 cents. A sale carries title to the land.

Deposits of pebble phosphate range in thickness from a few feet to 20 or 25 feet with an average of about 12 feet. The pebbles vary in color from light gray to black and in size from those smaller than a pin head to nodules almost as large as one's fist. The overburden which is chiefly sand ranges from a few feet to 40 feet in thickness with an average thickness of about 15 feet.

Hydraulic mining is almost universally employed in these fields and immense tonnages are thus readily and cheaply handled. Both steam shovels and hydraulic giants are used in removing the overburden from the pebble deposits, the operation often being so conducted that this overburden is used to fill in the pits of mined over property and thus make it possible at some future date to use such areas for agricultural purposes. After the overburden is removed the phosphate and matrix is excavated by hydraulic means. Heavy streams of water under a pressure of 100 to 160 pounds per square inch wash the banks of phosphate matrix down into a sump where it is sucked up by centrifugal pumps and conveyed through heavy 10 inch pipes to the washer plant. In deep mines or where the deposit is located at some distance from the washer a second pump or "booster" is often necessary in order to raise the material to the proper height.

The washing and screening processes are quite similar to those employed in the hard rock regions, but by the use of rotating and vibrating screens of smaller mesh, finer particles of phosphate are frequently saved. In a number of cases concentrating tables similar to those employed in washing metalliferous ores have been used. After the rock is washed and drained it is dried in rotary kilns (heated by oil burners) to a moisture content of one per cent. Several grades of pebble phosphate are marketed. The lower grades which are used chiefly for domestic consumption contain from 66 to 68 per cent tricalcium phosphate



FIG 3—Hydraulic Mining of Florida Pebble Phosphate



FIG 4—Removing Overburden from a Deposit of Florida Phosphate by Means of a Steam Shovel

deposits is such that a sharp, clean separation of the phosphate from its impurities can not be brought about by mechanical means.



FIG. 5—A Florida Phosphate Mine After the Removal of Overburden

Chemical or heat treatment of the mine run phosphate seems to offer the only solution to the problem of utilizing fully the phos-



FIG. 6—A Vast Pile of Washed Undried Public Phosphate

phoric acid present in these deposits. The most promising of these chemical processes appears to be the pyrolytic or volatilization meth-

od of producing phosphoric acid which is discussed in detail further on

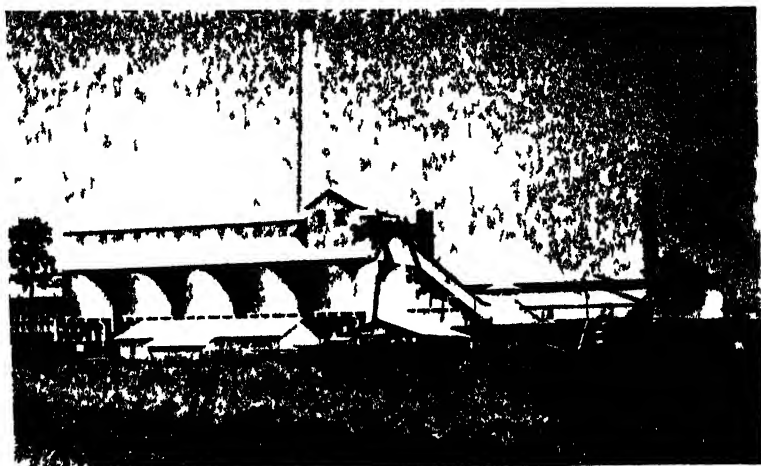


FIG. 7. A Phosphate Drying Plant and Storage Bins

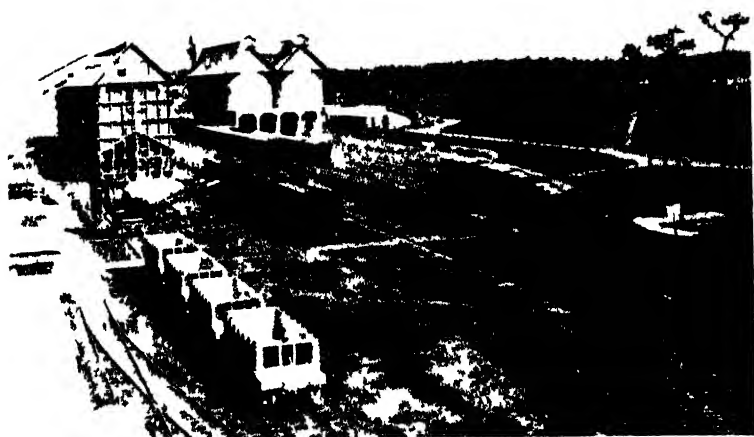


FIG. 8. Railroad Yards of a Phosphate Company in Florida

Since the pebble deposits of Florida are fairly regular in their occurrence, the range in the cost of preparing this type of phosphate for the

market is not as wide as that of producing the hard rock type. At the same time the present unsettled industrial conditions cause fluctuations in the prices of labor, fuel and equipment from time to time which



FIG. 9.—A Trainload of Pebble Phosphate En Route to Port Tampa, Florida.

make it difficult to estimate closely the average cost of production per ton. The following figures, Table VIII, however, compiled from data furnished by a number of large operators in the pebble fields may on the whole be regarded as fairly conservative.

TABLE VIII

AVERAGE COST (PER LONG TON) OF PRODUCING FLORIDA PEBBLE PHOSPHATE FOR THE MARKET

Items	Cost per Long Ton
	Dollars
Overburden removal*50
Mining and washing*75
Hauling and storing10
Drying*50
Depreciation15
Maintenance25
Insurance and taxes10
Interest at 6 per cent.15
Total†	2.50

* Including labor and power.

† Exclusive of overhead charges.

The soft phosphate of Florida occurs chiefly in the hard rock regions usually associated with the latter material, although the pebble phosphate deposits also contain appreciable quantities. This type of phosphate is, as its name implies, a plastic claylike substance when wet but can be readily disintegrated to a fine powder when dry. It is very high in alumina and therefore cannot be used in the manufacture of ordinary acid phosphate where the presence of this compound causes retrogression and gives the final product undesirable physical properties. Efforts have been made, however, to separate the soft phosphate from the other materials with which it occurs and dry and grind the product for direct application to the field. The material is in a very fine state of division and has, as a rule, a considerably greater solubility in certain conventional media designed to approximate the availability of phosphate materials under soil conditions. The expense of mining, separating and drying soft phosphate, however, is so great that the material must be sold at a price which discourages its general use, particularly since its agricultural value has not been proven beyond question. As placed upon the market soft phosphate contains approximately 25 per cent of phosphoric acid (P_2O_5).

The production, marketed output, domestic consumption and exportation of Florida phosphate for the past 10 years are given in Table IX.

TABLE IX
STATISTICS OF FLORIDA PHOSPHATE^a
(In long tons)

Year	Production				Total Shipments	Domestic Consignment	Exports
	Soft Phosphate	Hard Rock	Pebble	Total			
1914.....	309,689	1,787,597	2,138,891	2,138,891	1,130,764	928,993
1915.....	42,962	1,368,282	1,411,244	1,411,244	1,209,898	253,192
1916.....	81,071	1,601,061	1,682,132	1,520,706	1,158,052	203,435
1917.....	93,339	2,016,462	2,109,801	2,096,670	1,317,270	133,146
1918.....	17,736	42,840	2,141,950	2,202,526	2,067,230	1,963,524	122,336
1919.....	8,715	101,300	1,159,419	1,269,434	1,339,962	1,944,894	362,402
1920.....	13,953	400,249	2,955,182	3,369,384	3,355,431	977,560	1,038,251
1921.....	4,419	175,774	1,599,835	1,780,028	1,780,028	2,317,180	727,019
1922.....	446	121,485	1,895,415	2,017,346	2,058,593	1,053,009	574,951
1923 ^b	199,516	2,348,137	2,547,653	2,547,653	1,711,395	836,258
1924 ^b	143,115	2,289,466	2,432,581	2,336,000

^a U. S. Geol. Surv. ^b Marketed production.

Tennessee.

The phosphate deposits in this country which rank next to Florida in commercial importance are those of Tennessee. Much work has been done in these fields and numerous valuable historical, geological reports and technical articles published.¹⁹ A brief description of these deposits, their mode of occurrence and the systems of mining employed are given below, however, in order to show their economic relation to industries wherein this mineral is employed as a raw material; moreover the development of other processes of producing phosphoric acid makes it appear that the Tennessee phosphate fields will probably be the seat of profound changes in future fertilizer practice.

Tennessee is well situated for the distribution of fertilizer material to the southern and middle western states. Its phosphate deposits occur in what is known as the Central Basin of Tennessee (elevation 600 feet) and in the valleys of the western part of the Highland Rim (elevation 1,000 feet) surrounding this basin. The area covers approximately 7,000 square miles of gently undulating country but the phosphate deposits have been developed only in the western part of this area. The mines which are at present productive lie chiefly in Lewis, Maury, Hickman and Giles Counties, but deposits have also been mined in Davidson, Williamson, Perry and Decatur Counties. The main streams in the phosphate region are the Cumberland, Duck and Tennessee Rivers, but there are numerous creeks and tributaries of the Duck

¹⁹ For the history, geology, and description of the Tennessee phosphates see: Hayes, C. W., 16th Annual Rep. U. S. Geol. Survey, pt. 4, pp. 610-630 (1895); 17th Ann. Report (1896), pt. 2; 21st Ann. Rpt. (1901), pt. 3, U. S. Geol. Survey; Folios No. 90 (1903) and 95 (1903), U. S. Geol. Survey, Menninger, C. G., 16th Annual Report, U. S. Geol. Survey, pp. 631-635 (1895); Mineral Resources, U. S. Geol. Survey (1894-1921); Branner, J. C., The Phosphate Deposits of Tennessee, Trans. Amer. Inst. Mining Eng., Vol. 26 (1896), Eckel, B., Bull. 213, U. S. Geol. Survey (1903); Brown, L. P., Phosphate Deposits of the Southern States, Eng. Assoc. of the South Proc., 15, No. 2 (1904), Brown, L. P., The Phosphate Deposits of Continental N. America, 8th Int. Congress of Applied Chemistry, 26, pp. 87-113 (1912); Waggaman, W. H., Bull. 81, Bureau of Soils (1912); Maynard, T. P., White Rock Phosphates of Decatur Co., Resources of Tennessee, 3, pp. 161-169 (1913); Hook, J. S., Brown and Blue Phosphate Deposits of S. Central Tenn., Resources of Tenn., 4, pp. 51-56 (1914); Hook, J. S., The White Phosphates of Tennessee, Resources of Tenn., 5, pp. 23-33 (1915); Watkins, J. H., Phosphate Rock in Johnson County, Tennessee, Mining & Eng. World, p. 217, Aug. 7 (1915); Jenkins, O. P., Phosphates and Dolomites of Johnson Co., Tenn., Resources of Tenn., 6, pp. 51-106 (1916); Phalen, W. C., The Conservation of Phosphate Rock in Tennessee, Resources of Tennessee, 6, pp. 193-216 (1916); Barr, J. A., Use of Low Grade Phosphates, Bull. Amer. Inst. Mining Eng., Vol. 54, pp. 474-476 (1916); Mansfield, G. R., Phosphate Resources of the U. S., pp. 16-19 (1917); Smith, R. W., Mining and Washing Phosphate Rock in Tennessee, Eng. & Mining Jour. Press, Vol. 115, No. 5, pp. 221-226 (1923); Smith, R. W., Geology and Utilization of Tennessee Phosphate Rock, Trans. of Amer. Inst. Mining & Met. Engrs., Sept. (1924).

River that are of considerable importance as sources of water supply for mining and handling the rock. The phosphate area is served by three railroads affording excellent transportation facilities to the south east and middle west.

There are three economically important types of phosphate rock in Tennessee, namely, the brown, the blue and the white phosphate. The last mentioned type, however, is not being mined at present owing to its irregular occurrence and the pockety nature of the deposits.

Brown Rock Phosphate.—All of the Tennessee brown rock phosphate occurs in rocks of Ordovician Age but there are numerous phosphate horizons in this series which frequently occur so close together that they may be mined as a single bed. According to Hayes and Ulrich²⁰ the stratigraphic succession of these phosphate bearing formations are as follows: (Table X.)

TABLE X
GEOLOGIC FORMATIONS IN WEST-CENTRAL TENNESSEE WHICH CARRY
BROWN ROCK PHOSPHATE

Age	Formation	County Where Found
Ordovician	Leipers formation	Lewis, Hickman, Summer
	Catheys formation	Maury, Hickman (unimportant)
*
	Bigby limestone	Maury, Giles
	Hermitage formation	Maury, Williamson, Davidson

* According to R. W. Smith of the Tennessee Geological Survey, a formation known as the Cannon occurs between the Bigby and the Catheys formations which has given rise to several important phosphate deposits in Williamson and Davidson Counties.

The deposits of brown rock phosphate are generally conceded to be formed from phosphatic limestones by the leaching out of the more soluble carbonate of lime, the removal of the latter compound being attended by a diminution in thickness and a consequent settling of the phosphatic strata. Some secondary deposition has also taken place in the pores of the leached mother rock.

Two distinct forms of deposits have been recognized, namely, collar and blanket deposits. The first type occurs where the horizontal phosphatic limestone stratum outcrops on the slope of a steep hill. Under these conditions the parent rock has been leached only at the outcrop, the main stratum being protected from the action of percolating waters by the heavy overburden of more recent formations. This class of deposit has proved very deceptive in mining operations since the grade falls off rapidly as the stratum is followed into the hill. The blanket

²⁰ Columbia Folio No. 95, U. S. Geol. Survey (1903).

deposits on the other hand sometimes cover wide areas and usually lie near the surface of gently undulating hills where the underdrainage has been favorable to the leaching action of percolating waters. Almost ideal conditions exist in the Mt. Pleasant region (Maury County) for the formation of such deposits. The brown rock phosphate varies in color from a light gray to a deep chocolate brown and in texture from a porous rock disintegrating into phosphatic sand to a hard close grained rock quite resistant to weathering. On the average, however, the rock consists of brown or gray plates which form beds ranging in thickness from a few inches to 20 or 30 feet with an average of 6 to 8 feet. While the overburden also varies considerably from place to place there are few mines where the thickness is so great as to preclude its removal by steam shovel, drag line or hydraulic means.

For a number of years after the discovery of these deposits the mining methods employed were very crude and wasteful, no attempt being made to recover anything but the lump or plate rock, but during the last decade great advances have been made in the mining and handling of the brown rock phosphate and a far greater efficiency thus attained.

Under present conditions the overburden is first stripped by means of the steam shovel, drag line, scrapers, or hydraulic means and the phosphate strata thus exposed are mined mechanically although a little over one-third of the total is still produced by hand methods. The lump rock and fines are loaded into tram cars and hauled to the washer plants which are somewhat similar to those employed in the Florida phosphate fields. A flow sheet of a typical washer plant as furnished by Mr. James A. Barr of Mt. Pleasant, Tenn., is shown in Figure 10. The crude phosphate containing various impurities is first crushed and then proceeds to rock washers or rotating cylinders with shells that lift the material and then drop it with the object of breaking up the mud balls and so agitating the material that the fine clay and sand are suspended in water which is furnished to the logs or cylinders in large quantities. The water carrying this finer material in suspension goes to the fine sand recovery apparatus while the coarser settled material is discharged into some form of classifier, usually a trommel. The oversize from the classifier is then run upon a picking belt where chert, limestone and mud balls are removed by hand. The undersize from the classifier goes to the sand recovery apparatus. This latter equipment consists of a series of inverted pyramids (Allen cones), cylindrical jet washers or a combination of these washing devices. The clay and the finer sand are carried away by the overflow to the fine sand recovery apparatus while the heavier sand settles to the bottom of the vessels, where a jet of clean water carries it up through a pipe to the next tank

where it is further cleansed. Finally, the material is conveyed to some dewatering device such as Dorr classifiers, Allen dewatering cones or plain drag classifiers. The underflow from this goes to the wet storage pile. The equipment for the treatment of the very fine sand consists of more Allen cones or Dorr thickeners. The overflow from the treatment of the very fine particles of phosphate is discharged into the set-

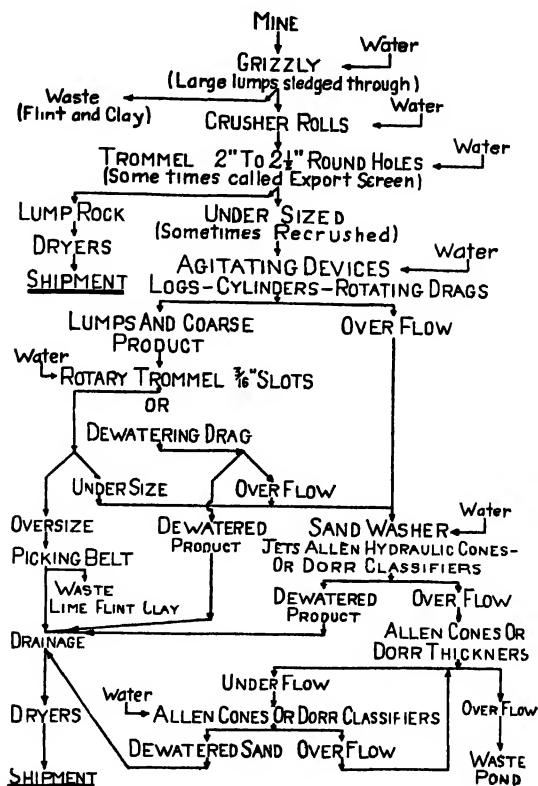


FIG 10 - Flow Sheet of Tennessee Phosphate Washer

ting ponds while the underflow goes to dewatering devices, where it receives further cleansing and is finally taken up by conveyers and placed in wet storage. Nearly all of the brown phosphate rock produced today is dried in rotary kilns similar to those used in the Florida pebble fields, but a small tonnage of lump rock is still either sun dried, or piled on ricks of wood in open sheds and the burning conducted by the method used in the old pioneer days of this industry.

Most of the brown rock phosphate mined in Tennessee is disposed of

in this country and while the better grades of material will analyze as high as 78 per cent tricalcium phosphate the average grade is about 72 per cent with 5 per cent combined oxides of iron and aluminum. Some of the lower grades analyzing 60 per cent tricalcium phosphate and containing relatively large amounts of iron and aluminum oxides are very finely ground and sold for direct application to the soil.

While the efficient mining of brown rock phosphate involves the outlay of considerable capital, the percentage of recovery by the use of modern mechanical equipment is so much greater than it was in the former days when the value of the phosphate sand was unknown or unappreciated, that the cost of production has been maintained at a relatively low figure. Moreover, were it not for this mechanical equipment the Tennessee brown phosphate fields must have been largely abandoned by this time owing to the exhaustion of the bulk of the high grade lump rock. While the present cost of production varies considerably from place to place, being effected very greatly by the amount and character of the overburden as well as the thickness and richness of the deposits, the following figures (Table XI) may be regarded as conservative and roughly approximating the average cost per long ton of producing this material:

TABLE XI
AVERAGE COST (PER LONG TON) OF PRODUCING TENNESSEE BROWN
ROCK PHOSPHATE

Items	Cost per Long Ton
	Dollars
Labor *	1.50
Drying rock (fuel)40
Depreciation on land50
Depreciation on plant25
Power (electric or steam)50
Shipping10
Maintenance45
Taxes and insurance10
Interest at 6 per cent15
Total †	3.95

* Includes labor for mining, washing, drying and storing.

† Exclusive of overhead charges.

R. W. Smith ²¹ gives the following brief but clear description of the method employed in prospecting for brown phosphate rock:

"Because of the irregular character of the brown phosphate deposits, careful prospecting is necessary before development. The area to be

²¹ Geology and Utilization of Tennessee Phosphate Rock, Trans. of American Institute of Mining and Met. Engineers, Sept., 1923.

prospected is laid off in 50-foot or 100-foot squares, and at the intersection of each square a hole is put down to the limestone by means of a post-hole auger. By examining the material brought up, the thickness of the over-burden and of the phosphate is determined. The sample of phosphate thus obtained is washed in as many changes of water as seems necessary to approximate the conditions of a phosphate washer and, after drying, is analyzed. At certain determined places in the phosphate area thus blocked out, pits are sunk to the bottom of the phosphate. From each pit, a sample 1 ft. square and the thickness of the entire phosphate layer is taken. This is washed in tubs, approximating as nearly as possible the conditions of a phosphate washer, and the resulting washed phosphate is weighed. The weight divided by the thickness will give the recovery per cubic foot. The average recovery per cubic foot multiplied by the area, in square feet, underlain by commercial phosphate multiplied by the average thickness of the phosphate in this area, all divided by 2,240 lbs., will give the tonnage of phosphate that may be recovered from the area."

The mechanical handling and washing of Tennessee brown phosphate has reached such a high degree of efficiency that it is hard to conceive how it may be improved. In spite of exercise of the greatest care, however, and the saving of very fine phosphate sands, the wash waters carry away large quantities of this mineral in suspension. It is generally conceded, therefore, that an absolute sharp separation of the phosphate from the matrix cannot be effected by mechanical devices and this has led to investigations of chemical methods and heat processes whereby a fuller utilization of the phosphoric acid in these natural deposits might be effected. The work which has been conducted on the run-of-mine phosphates from the brown rock area is discussed in detail further on in this publication.

Blue Phosphate. The important deposits of blue rock or Devonian phosphate in Tennessee lie along Leatherwood Creek in the western part of Maury County, south and east of Centerville on both sides of Swan Creek in Hickman County and in the eastern part of Lewis County near the village of Gordonsburg. The most important mines now being exploited are in Hickman and Lewis Counties. The blue phosphate, according to Hayes and Ulrich,²² is a conglomerate deposit derived in part from the underlying Ordovician limestone and partly from the remains of marine life which were more highly phosphatic than those of the Ordovician period, and consequently the deposits required little or no subsequent leaching to make them of economic value. This type of phosphate occurs in distinct strata which are blue, black or gray in color and range in texture from hard massive close grained rock to

²² Loc. cit.

coarsely oolitic material which is rather readily broken up. In general the phosphate bearing formation may be described as a bluish gray rock composed of flattened ovules and the water worn casts of phosphatic shells which weathers on exposure to a rusty yellow. The thickness of the beds vary from a few inches to 4 feet, but any stratum less than 18 inches in thickness is hardly considered worth mining. The phosphate stratum is overlain by a massive blue black shale or slate 3 feet or more

TABLE XII

ANALYSES AND DESCRIPTIONS OF PHOSPHATE BEDS FROM LOCALITIES WHERE THE BLUE OR DEVONIAN ROCK DIRECTLY OVERLIES THE BROWN OR ORDOVICIAN PHOSPHATE

Sample No	Location	Thickness of Strata	Description	Analyses	
				P ₂ O ₅	Ca ₃ (PO ₄) ₂
68	Mine 6 miles S E. of Centerville, Tenn	0' 9"	Coarse hard blue rock	24 80	54 20
69	"	0' 9"	Fine grained blue rock	27 91	60 99
70	"	2' 6"	Coarse oolitic gray rock	35 79	78 21
60	Mine 8 miles east of Centerville, Tenn	1' 3"	Close grained hard blue rock	25 25	55 18
61	"	0' 8"	Brown disintegrated phosphate	32 95	72 01
66	"	1' 6"	Coarse oolitic blue rock	32 40	70 82
71	Mine 2 miles south of Centerville, Tenn	1' 8"	Fine grained hard blue rock	26 44	57 79
72	"	1' 2"	Fine grained hard blue rock	36 66	80 11
*		Brown phosphate	

* No sample collected

in thickness and it is, therefore, generally necessary to use underground methods of mining. Main tunnels are driven from the surface into the phosphate and at regular intervals rooms about 25 to 50 feet in width are turned off at right angles leaving pillars for the support of the overlying formations. Since the blue shale or slate directly overlying the phosphate forms as a rule an excellent roof no great amount of timbering is required in these mines. Practically all of this rock is mined by drilling, and blasting, the slabs or lumps being subsequently broken

up by sledges and loaded by pick or shovel. While this type of phosphate requires no washing and is by no means as porous as the brown rock phosphate, it contains comparatively little moisture and some miners do not consider it essential to dry the material. Where the moisture content is appreciable, however, it is dried either on ricks of wood or in rotary kilns. Although some specimens of blue rock phosphate run as high as 78 to 80 per cent bone phosphate of lime the average grade of the rock is not usually more than 68 per cent. The iron and aluminum present may or may not be higher than that in the average



FIG. 11 Phosphate Mining in Tennessee. A Dragline Used for Removing Overburden from Deposits of Brown Rock Phosphate

grade of the brown rock phosphate. The cost of producing this type of phosphate is not far from that of extracting a marketable grade of brown rock, for though the phosphate strata are usually considerably thinner than the beds of brown phosphate, no costly washing equipment is required and a clean separation of the phosphate from the underlying and overlying formations can be more readily effected.

In a number of localities an unconformity exists, which brings the Devonian or blue phosphate directly over the brown or Ordovician rock. Under these conditions mining may be conducted quite profitably.

The analyses of some typical sections of phosphate from areas where such conditions occur are given in Table XII.

The White Phosphates.—The white phosphates of Tennessee so far exploited occur in Perry and Decatur Counties on both sides of the Tennessee River. These phosphates are all of secondary origin and are

divided by Hayes ²⁸ into three classes, namely, the stony, breccia and lamellar varieties, the last mentioned is the richest and apparently the most plentiful. Much of the white phosphate of Tennessee resembles the hard rock phosphate of Florida, and occurs in irregular pockets along with clay and other foreign material. The breccia variety consists of chert fragments imbedded in a matrix of high grade phosphate, while the stony phosphate consists of silicious skeletons formerly filled with carbonate of lime, but now containing phosphate. Both of these varieties must be separated from the associated chert in order to yield



FIG 12.—Cantilever Mining Machine for Handling Brown Rock Phosphate and Matrix After the Overburden Has Been Stripped

a commercial product, and up to the present the cost of effecting such a separation has been considered too great to warrant the exploitation of these two varieties of white phosphate. The lamellar variety of white phosphate, however, is a very high grade material—occurring in plates of various thickness, which are frequently cemented together forming large boulders. The rock as a whole is close grained, very hard, and often coated with a thin lustrous layer of precipitated phosphate. Picked samples of the lamellar phosphate may contain as high as 85 to 90 per cent bone phosphate of lime and it has been mined in carload lots containing from 72 to 78 per cent of this ingredient.

While no development work is being conducted in the white phosphate fields at the present time, the rock was formerly mined by both

²⁸ Mineral Resources, U S Geol Survey, part 4, pp 623-630 (1894-1895); Ann. Report, U. S Geol Survey (1899-1900), part III, pp. 484-485; Ann. Report, U. S. Geol. Survey, Part II, pp. 236-250 (1895-1896).

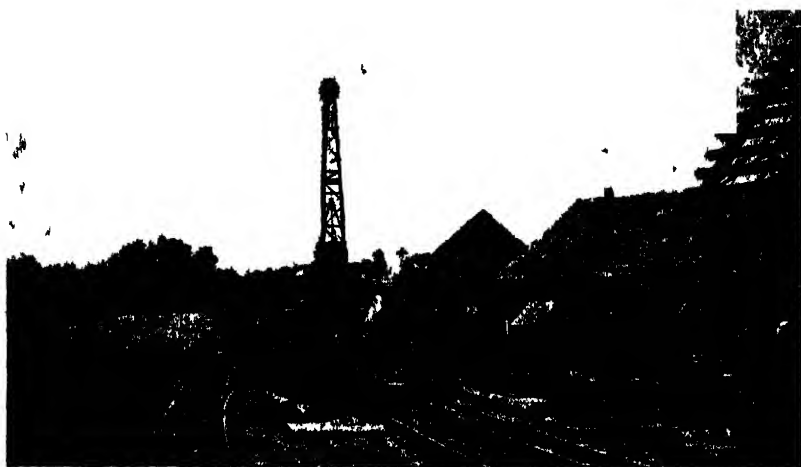


FIG. 13.—Preparing Tennessee Brown Rock for the Market Dumping the Phosphate and Matrix into "Skips" Preparatory to Washing the Rock.



FIG. 14.—A Modern Tennessee Phosphate Washer and Drying Plant.

open cut and by tunnelling. The former method was employed wherever the character and depth of the overburden would permit, but the overload was frequently so heavy as to render its removal impracticable and

under these conditions tunnelling was resorted to. Owing to the loose character of the overlying clay, extensive timbering was required, which added considerable to the cost of production.

On account of the uncertain character of these deposits, the careful prospecting necessary in order to determine their value and extent, and a number of other factors which tend to make mining operations costly, the exploitation of the Tennessee white phosphates ceased in 1908. Spasmodic efforts have been made to revive this industry, but it seems doubtful if the development of this class of rock will be again taken up until the large, accessible and more uniform beds of high grade Tennessee brown and blue phosphate have become depleted.

Views of mining operations in the Tennessee phosphate fields are shown in Figures 11, 12, 13 and 14.

Utah, Idaho, Wyoming and Montana.

The most extensive phosphate deposits yet discovered occur in the western part of the United States, and underlie immense areas in southeast Idaho, western Wyoming, northern Utah, and western Montana. The deposits have been mined and developed to a limited extent in southeast Idaho, near the little towns of Soda Springs, Georgetown and Montpelier on the Oregon Short Line Railroad; near Paris, Idaho, several miles distant from the same railroad; along the west front of the Sublette Mountain Range, near Border Station on the Idaho-Wyoming border; at the south end of the same mountain range about one and one-half miles from Cokeville, Wyoming, which is also on the Oregon Short Line Railroad; in southwest Wyoming, and in Northern Utah along the western front of the Crawford Mountains, about 6 miles from Sage Station, Wyoming. Very little development has been done in Montana but the phosphate has been recognized near Melrose, Montana, a town on the Oregon Short Line Railroad, and also at Garrison, Phillipsburg, and Cardwell on the Northern Pacific Railroad from 40 to 70 miles north of Melrose.

The geology, topographic features and economic possibilities of the western phosphates have been ably described and discussed by a number of investigators²⁴ so only a brief summary of these deposits is given below.

²⁴For the history, geology, and description of the Western Phosphates, see: Weeks, F. B., and Ferrier, W. F., Bull. 315, U. S. Geol. Survey, pp. 449-462 (1907); Weeks, F. B., Bull. 340, U. S. Geol. Survey, pp. 441-447 (1908); Girty, G. H., Bull. 436, U. S. Geol. Survey (1910); Gale, H. S., and Richards, R. W., Bull. 430, pp. 457-535 (1910); Waggaman, W. H., Bull. 69, Bureau of Soils (1910); Blackwelder, E., Bull. 430, U. S. Geol. Survey (1910); Blackwelder, E., Bull. 470, U. S. Geol. Survey, pp. 452-481 (1911); Richards, R. W., and Mans-

The Western phosphates are generally regarded as original sedimentary deposits laid down when that portion of the earth's surface was submerged in water. The phosphate is of Carboniferous age and occurs in both Mississippian and Permian rocks but the deposits in the latter formation have so far proven to be of the greatest commercial importance.

The topography of much of this area is extremely rugged, the phosphate and associated strata being folded, faulted and subjected to intense erosion. As Mansfield²⁵ states, however, the phosphate owes its exposure to these disturbing and erosive processes, for otherwise it would be buried by the accumulations of later sediments.

These phosphates are quite distinct in their mode of occurrence and physical properties from those found in Florida or South Carolina and quite unlike the Brown rock deposits of Tennessee. They more nearly resemble the so-called blue phosphate of the last mentioned state though the beds are much thicker. The deposits on the whole consist of gray to black rock varying considerably in hardness and ranging from fine grained to coarsely coltic in texture. The richer beds are from 2 to 6 feet in thickness and contain from 65 to 75 per cent of bone phosphate of lime and less than 3 per cent of the combined oxides of iron and aluminum. The better beds of phosphate are interstratified with limestones and shales which have as yet been regarded as of little commercial significance though some of them contain relatively high percentages of P_2O_5 .

The following (Table XIII) is a complete section of phosphate bearing strata which was exposed in Georgetown Canyon, Idaho, and sampled and analyzed by the author.²⁶

field, G. R., Bull. 470, U. S. Geol. Survey, pp. 371-439 (1911); Gale, H. S., Bull. 470, U. S. Geol. Survey, pp. 440-451 (1911); Richter, A., A Western Phosphate Discovery, Mines and Minerals, Vol. 2, No. 9, p. 207 (1911); Brown, L. P., Phosphate Deposits of Continental N. America, 8th Int. Congress of Applied Chem., 26 (1912); Shultz, A. R., and Richards, R. W., Bull. 530, U. S. Geol. Survey, pp. 267-281 (1913); Pardee, J. T., Bull. 530, U. S. Geol. Survey, pp. 285-291 (1913); Richards, R. W., and Mansfield, G. R., Bull. 577, U. S. Geol. Survey (1914), Shultz, A. R., Bull. 543, U. S. Geol. Survey, pp. 131-134 (1914); Jones, C. C., A New Phosphate Field in the U. S., Trans. Amer. Inst. Min. Engr., 47, pp. 192-216 (1914); Stone, R. W., and Bonine, C. A., Bull. 580, U. S. Geol. Survey, pp. 373-383 (1914); Mansfield, G. R., Bull. 620, U. S. Geol. Survey, pp. 331-349 (1916); Mansfield, G. R., The Phosphate Resources of the United States, Second Pan American Scientific Congress, Washington, U. S. A., pp. 21-36 (1917); Schultz, A. R., Bull. 680, U. S. Geol. Survey (1918); Mansfield, G. R., Origin of the Western Phosphates, Amer. Jour. of Sci., 46, pp. 591-598 (1918); Mansfield, G. R., Bull. 713, U. S. Geol. Survey (1920).

²⁵ The Phosphate Resources of the United States, Second Pan American Scientific Congress, p. 23 (1917).

²⁶ Waggaman, W. H., A Review of the Phosphate Fields of Idaho, Utah and Wyoming, Bull. 69, Bureau of Soils, U. S. Dept. of Agriculture (1910).

TABLE XIII

SECTION OF BASAL PORTION OF PHOSPHORIA FORMATION IN GEORGETOWN CANYON
(SE. ¼ NW. ¼ SEC. 30, T. 10 S., R. 45 E. OF THE BOISE MERIDIAN), IDAHO

(Land lines theoretical)

Field No. of Specimen		P ₂ O ₅	Equiva- lent to Ca ₃ (PO ₄) ₂	Thick- ness
		Per Cent	Per Cent	Ft. In.
144-A	Shale, calcareous, or muddy limestone, brown, weathering into irregular chip fragments, effervesces vigorously.....	3.5	7.7	25 6
144-B	Phosphate rock, oolitic, weathering brown or gray; effervesces slightly, lower 1½ inches somewhat cherty....	35.8	78.4	6
144-C	Shale, hard, brown, calcareous at the top, effervesces vigorously ..	Trace	1
144-D	Phosphate rock, coarsely oolitic, gray, effervesces vigorously	37.6	82.1	2 11
144-E	Shale, brownish, earthy, containing 6 inches of phosphate, effervesces considerably	10.0	21.9	1 0
144-F	Phosphate rock, including—			
	Phosphate rock, oolitic, hard, gray, calcareous	7		
	Phosphate rock, medium, gray, oolitic	6		
	Shale, phosphatic, light brown .. (Sample shows considerable effervescence)	4		
		21.9	48.0	1 5
144-G	Phosphate rock, including—			
	Phosphate rock, coarsely oolitic, gray, brittle	1		
	Phosphate rock, finely oolitic, brownish gray	4		
	Phosphate rock, coarsely oolitic, dark gray	2		
	Phosphate rock, finely oolitic, brownish gray	4		
	Phosphate rock, coarsely oolitic, gray	7		
	Phosphate rock, finely oolitic, thin bedded	3		
	Phosphate rock, coarsely oolitic, gray	1		
	(Sample effervesces slightly)			
144-H	Phosphate rock, including—			
	Phosphate rock, medium to finely oolitic, brownish gray ..	7		
	Shale, phosphatic, brownish, somewhat oolitic ..	10		
	Phosphate rock, coarsely oolitic.	2		
	Phosphate rock, shaly brown	3		
		29.3	65.3	1 10

TABLE XIII—(Continued)

Field No. of Specimen		P ₂ O ₅	Equiva- lent to Ca ₃ (PO ₄) ₂	Thick- ness
		Per Cent	Per Cent	Ft. In.
144-I	Phosphate rock, including—			
	Phosphate rock, coarsely oolitic, brownish-black streaks 1 1			
	Phosphate rock, shale, brown, thin bedded 5	34.7	75.8	4 10
	Phosphate rock, coarsely oolitic, crumbly 4			
	Phosphate rock, medium to coarsely oolitic 3			
	(Sample effervesces consider- ably.)			
144-K	Shale, brownish to black, earthy compo- sition, thin bedded, with a few lime- stone lenses, effervesces slightly.....	24.2	53.0	8 9
	Limestone, dark, compact, fetid.....	1 9
144-L	Shale, brownish to black, earthy; ef- fervesces slightly	11.7	25.6	12 0
144-M	Shale, including—			
	Shale, brownish black, earthy... 7			
	Concealed, not included in sam- ple (probably same as bed just above and below)... .. 4 7	15.1	33.1	17 0
	Shale, brownish black, earthy... 5 5			
144-N	Shale, black, earthy; effervesces slightly	19.9	43.6	12 0
144-O	Shale, brownish black, earthy... 4			
	Limestone, single stratum (not sampled) 2	21.2	46.4	12 0
	Shale, brownish black, earthy ... 4			
	Limestone, single stratum (not sampled) 2			
144-P	Shale, black and dark brown, calcareous, earthy, effervesces considerably ..	25.8	56.3	6 2
144-Q	Shale, black and dark brown, calcareous, earthy, effervesces considerably	24.6	53.9	12 0
144-R	Limestone, shaly, brownish gray, ef- fervesces vigorously	17.8	39.0	4 10
	Limestone, single stratum	11
	Limestone ("cap lime"), fine, dark gray, fossiliferous	2 3
144-S	Phosphate rock, main bed prospected, coarse to medium, oolitic, gray; con- tains two or more minor streaks of shaly material; effervesces slightly ...	36.8	80.4	6 4
144-T	Shale, brown, earthy; effervesces slightly	3.7	8.1	9
	Limestone, massive, underlying the phos- phatic series. Thickness not deter- mined.			
				139 11

From the data given in Table XIII, one can form some idea of the immense tonnages of low and medium grade phosphate contained in the western field, particularly when we consider that the quality of available high grade phosphate rock (65 per cent or better) is estimated at over 5,000,000,000 tons. But unless some method is employed other than that of treating the rock with sulphuric acid much of the lower grade material will be wasted since it is too high in calcium carbonate or iron and aluminum for the manufacture of acid phosphate and under present mining practice is discarded and lost when the higher grade strata have been removed.

The nature and occurrence of the western phosphates are such that they are mined (as a rule) by underground methods which are somewhat costly because of the timber required in the tunnels or drifts. But on the other hand, the rock being in bedded deposits and fairly free from moisture may be shipped directly without the necessity of washing or drying.

The great distance of the western phosphate area from the fertilizer market has so far prevented the extensive development of these deposits. It is only a question of time, however, before the demand for fertilizers will extend to the immense areas of agricultural land west of the Mississippi River and when this time arrives the western phosphates will be actively exploited. While a small tonnage is finely ground and used for direct application to the soil in certain citrus fruit sections of California, the most promising method of marketing the western phosphates so far employed is that practiced by a large copper smelter in Montana which has an immense potential production of sulfuric acid. This acid being a by-product from the roasting of sulfide ores can be manufactured at a low cost and used for making double superphosphate which contains from 40 to 45 per cent of P_2O_5 , as against 16 to 18 per cent of P_2O_5 in the ordinary acid phosphate of commerce. A product of this high concentration can stand the expense of the long freight hauls necessary to reach the fertilizer market. Probably an even more promising means of developing the western phosphates is the more general adoption of the pyrolytic or volatilization method of producing phosphoric acid. This process which may be carried on either in an electric or fuel fired furnace has the advantage of producing directly from medium or low grade rock relatively pure phosphoric acid of a high concentration. Since cheap coal is available in the western phosphate regions and there is every reason to expect further development of hydro-electric power, the pyrolytic process offers attractive possibilities.

South Carolina.²⁷

The phosphate area of South Carolina lies along the coast in a belt which in places is fully 20 miles wide, extending from the Wando River in Charleston County to the Broad River in Beaufort County. The coast region as a whole is but little above tide level and is intersected with numerous creeks, rivers and arms of the sea, therefore the phosphate area not only has excellent rail transportation facilities but large vessels can be loaded close to the mines and the phosphate shipped directly by water either to foreign ports or to Charleston where many fertilizer factories are located.

The South Carolina phosphate deposits were formerly classified under two heads, namely, "River Rock" and "Land Rock." The former was at first the most easily and eagerly exploited since it was dredged from the beds of streams and was fairly free from objectionable impurities. When a satisfactory method of cleaning the Land Rock was devised these latter deposits were rapidly developed and the mining of River Rock finally abandoned. These two types of deposits, however, are composed of the same material, the River Rock being merely the Land Rock washed down and concentrated in the beds of streams. The South Carolina phosphates belong to the Tertiary Period and are derived according to Rogers²⁸ from the Edisto Marl which is believed to be of Miocene Age. The rock occurs as boulders, nodules and small pebbles imbedded in a matrix of sand and clay. These nodules or boulders which range in color from light gray to black, are of medium hardness and are frequently much pitted, the pits being filled with clay or other foreign material which must be removed by washing in order to obtain a product sufficiently high grade for acid treatment.

²⁷ For the history, geology, and description of the S. Carolina phosphates see: Holmes, F. S., *S. Carolina Agriculturist* (1844); Toumey, *Geology of S. Carolina* (1848); Pratt, N. A., *Native Bone Phosphates of S. Carolina* (1868); Holmes, F. S., *Phosphate Rocks of S. Carolina* (1880); Shepard, C. U., *South Carolina Phosphates* (1880); Moses, O. A., *The Phosphate Deposits of S. Carolina*, Mineral Resources, pp. 504-521, U. S. Geol. Survey (1883); Penrose, A. F., Jr., *Nature and Origin of Deposits of Phosphate of Lime*, U. S. Geol. Survey, Bull. 46, pp. 60-70 (1888); Wyatt, Francis, *Phosphates of America* (187 pages) (1891); Levat, *Industrie des Phosphates et Superphosphates*, pp. 83-90, Paris (1895); Miller, C. C. II, *Florida, S. Carolina, and Canadian Phosphates*, 223 pages (1892); Wright, Carroll D., *The Phosphate Industry of the U. S.*, 6th Special Report of the Commissioner of Labor, Washington, D. C., pp. 23-69 (1893); Brown, L. P., *Phosphate Deposits of the Southern States*, Eng. Assoc. of the South, Proc. 15, No. 2 (1904); Brown, L. P., *The Phosphate Deposits of Continental N. America*, 8th Int. Congress of Applied Chem., 26 (1912); Waggonman, W. H., Bull. 18, U. S. Dept. Agric. (1913); Rogers, G. S., *The Phosphate Deposits of S. Carolina*, Bull. 580 of U. S. Geol. Survey (1914); Mineral Resources, U. S. Geol. Survey (1890-1921); Mansfield, G. R., *The Phosphate Resources of the U. S.*, pp. 6-8 (1917).

²⁸ Loc. cit.

The washing process employed in separating the phosphate from this foreign material is very similar to that used in the Florida Hard Rock fields.

The South Carolina phosphate beds, however, have an average thickness of only about one foot and hence mining operations are considerably more costly than in the Florida pebble fields where the deposits are in some instances 30 feet in thickness. On the other hand the recovery of rock per ton of material handled is as a rule, higher, and the losses of phosphate entailed in washing the South Carolina rock are not as great as in preparing Florida pebble for the market. After washing and drying the average grade of South Carolina rock is about 61 per cent bone phosphate of lime with a low content of iron and aluminum oxides.

These deposits were first exploited in 1868 and for many years furnished the bulk of our supply of phosphate rock and much of Europe's. During the early development of these fields some of the rock was finely ground and sold for direct application to the soil but practically all the rock produced in the past thirty years has been consumed in the manufacture of acid phosphate or double superphosphate, a product which is described in detail in a subsequent chapter.

Until recent years there was still a demand for South Carolina phosphate by certain foreign consumers who were familiar with its acidulation and had found that it gave a very satisfactory product. Much of the foreign demand for mineral phosphates is now being supplied, however, from the phosphate deposits of northern Africa.

The peak of production in South Carolina was reached in 1893 when 618,569 tons of phosphate rock were marketed, but since that date the output has gradually declined due chiefly to the discovery and development of the higher grade and more cheaply mined phosphate deposits of Florida and Tennessee. In 1921, owing to the depressed condition of the fertilizer industry, mining operations in South Carolina ceased entirely and in 1922 only 1,500 tons were marketed.

Contrary to general opinion, however, the phosphates of South Carolina are far from exhausted, and since there is considerable capital invested in mining and washing equipment in this field there is every reason to expect that mining operations will be resumed when market conditions improve. The quantity of minable phosphate still remaining in South Carolina has been variously estimated at from 9,000,000 to 11,000,000 long tons.²⁹

²⁹ Phalen, W. C., *The Conservation of Phosphate Rock in the United States*, Second Pan American Scientific Congress (Dec, 1915); Waggaman, W. H., *The Reserve Supply of Phosphate Rock in the United States*, *J. Ind. & Eng. Chem.*, Vol. 6, p. 464 (1914).

Kentucky Phosphate.⁸⁰

The phosphatic nature of certain limestones in Kentucky was first recognized in 1877 by Dr. Robert Peter,⁸¹ chemist of the Kentucky Geological Survey. This author described a thin layer of highly phosphatic limestone occurring in the "Lower Silurian" (Ordovician) near Lexington. The samples collected and analyzed, however, indicated that the phosphate rock was too uncertain in its composition and too irregularly distributed among the poorer limestones to be of any great commercial value.

Attention was again called to the presence of phosphate layers at the top of the so-called Trenton Limestone by A. M. Miller,⁸² as early as 1896 and again in 1904, when this geologist was engaged in some field work in Jessamine, Woodford and Franklin Counties. It was not until 1905, however, that active interest was taken in the Kentucky phosphate and actual development work was only begun five or six years later.

The phosphate deposits of Kentucky have so far proven of rather limited value and extent. Prospecting work has been carried on intermittently at various points of Fayette, Woodford, Scott and Jessamine Counties, but only in Woodford County has any quantity of the material been mined. The Kentucky phosphate region forms part of the great Cincinnati agricultural line extending from Nashville, Tennessee, in a northeasterly direction through Lexington County, almost to Cincinnati. South of this city it divides into two broad domes, one culminating near Nashville and the other in Jessamine County, Kentucky. The latter is known as the Jessamine Dome. All of the exposed rocks of these regions are of sedimentary origin and the arching of the strata took place so gradually that the horizontal position of the rocks is but little altered.

The following description of the geological occurrence and origin

⁸⁰ Ky. Geol. Survey Chem. Analyses A (1877), pp. 65-66.

⁸¹ Peter, Robt., Ky. Geol. Survey Chem. Analyses A, Part 1 (1890), p. 246; Ky. Geol. Survey, Chem. Analyses A (1877), pp. 65-66; Waggaman, W. H., Report on the Natural Phosphates of Tennessee, Kentucky and Arkansas, Bull. 81, Bureau of Soils, U. S. Dept. Agriculture (1912), Gardner, James H., Rock Phosphate in Kentucky, Mines & Minerals, Nov (1912), pp. 207-209; Miller, A. M., Geology of the Georgetown Quadrangle; Ky. Geol. Survey Series 4, Vol. 1, part 1 (1913), pp. 317-364, Foerste, A. E., The Phosphate Deposits in the Upper Trenton Limestones of Central Kentucky, Ky. Geol. Survey series 4, Vol. 1, part 1 (1913), pp. 391-439; Phalen, W. C., Phosphate Rocks in Central Kentucky, Ky. Geol. Survey (1915), 80 pages.

⁸² The Association of the Gastropod Genus *Cyclora* with Phosphate of Lime Deposits, Amer. Geologist, Vol. 17, pp. 74-76 (1896).

of the Kentucky phosphate is abstracted from the report of W. C. Phalen.²¹

"The country rocks associated with the phosphate rock deposits are all limestones of different lithology and degrees of purity. They are all of marine origin and belong to the middle part of the Ordovician system; their total thickness is approximately 330 feet.

"The rock of Central Kentucky belongs entirely in a class known as brown phosphate, first so-called in middle Tennessee. It occurs as a distinctly laminated residual deposit, also as filling solution cavities or pockets in a more or less phosphatic limestone. The rock itself occurs in porous or loosely coherent plates, varying in thickness from the very thinnest up to those several inches thick. Usually the plates are separated from each other by layers of loosely cemented or porous material consisting of phosphate rock in a fine state of division, mixed with more or less clay. There is also another form of brown rock, known as phosphate sand, some of which is very rich in calcium phosphate."

TABLE XIV
COMPOSITION OF DIFFERENT TYPES OF KENTUCKY PHOSPHATE

Sample No.	Location	Description	Analyses			
			SiO ₂	$\frac{Fe_2O_3 + Al_2O_3}{Al_2O_3}$	P ₂ O ₅	$\frac{Ca}{(P \times 4)}$
200	Near Midway, Ky.	Light yellow, soft	24 29	17 18	21 34	46 71
201	" " "	Dark brown, close grained plates	2 63	2 75	35 71	78 17
202	" " "	Dark brown, porous hard	4 88	3 67	34 00	74 43

While individual samples of Kentucky phosphate have analyzed as high as 78 per cent tricalcium phosphate, the average grade of the rock is probably considerably below that found in Tennessee. Analyses of a number of types are given in Table XIV.

Owing to the presence of so much finely divided foreign material, Kentucky phosphate must be washed in order to obtain a product suitable for the manufacture of acid phosphate if any considerable tonnage is to be obtained from the deposits. An appreciable tonnage of this material of lower grade (60 per cent tricalcium phosphate) has been finely ground and sold for direct application to the soil.

On certain farms in the vicinity of Wallace and Midway, Kentucky, a little mining has been conducted for a number of years and an average grade of rock containing 72 per cent bone phosphate of lime, re-

²¹ Phosphate Rocks of Central Kentucky, Ky. Geol. Survey (1915), 80 pages.

covered and milled at a small plant located at the former place—the coarser lumps being used for the manufacture of acid phosphate and the finely ground material is sacked and sold as raw rock for direct application to the field. One washing plant has been erected at Versailles, Ky., to recover the finely divided phosphate, such as saved in the Tennessee fields.

Arkansas Phosphate.³⁴

These phosphate deposits are not generally regarded as of much economic importance since compared with the product of Florida, Tennessee, the western States, and even South Carolina, the rock is of a low grade.

The deposits, however, are well situated to supply the growing demand for fertilizers west of the Mississippi River and though much of the material is too low in P_2O_5 and too high in iron to make it desirable for the manufacture of acid phosphate by the sulfuric acid process, the development of the pyrolitic method of producing phosphoric acid may result in the renewal of mining activity in these fields.

While mention is made of the occurrence of phosphate in a number of localities in Searcy, Izard, Stone, Marion, Baxter and Boone counties, the rock has been developed only in the Northwestern part of Independence county along Lafferty Creek north and west of the White River and about 10 miles from Batesville.

The developed deposits of phosphate in Arkansas were formerly considered of Devonian age,³⁵ but more recent investigations have shown them to be older. The rocks of the phosphate horizon vary considerably in character, but there are always bands of shale occurring among the phosphate strata. Manganese ore is also closely associated with the phosphate in many places, much of the rock being stained by this substance.³⁶

The phosphate in the developed area occurs in two strata—one directly overlying the other. The first or upper layer is from $3\frac{1}{2}$ to 6 feet in thickness and consists of a hard massive rock made up of the rounded fragments of organic débris closely cemented together. It varies in color from light gray to brownish black, the color largely depending on the quantities of iron and manganese present. This bed

³⁴ Branner, *Amer. Inst. Min. Engrs.*, Vol. 26 (1896); Branner and Newson, *Bull. 74, Ark. Agric. Exper. Sta.* (1902); Purdue, *Bull. 315, U. S. Geol. Survey*, pp. 463-473 (1907); Waggaman, W. H., *Bull. 81, Bureau of Soils* (1912), pp. 30-36.

³⁵ Branner, *Amer. Inst. of Min. Engrs.*, Vol. 26 (1896); Branner and Newson, *Bull. 74, Ark. Exp. Sta.* (1903).

³⁶ Purdue, *Bull. 315, U. S. Geol. Survey*, pp. 463-473 (1907).

averages from 55 to 60 per cent bone phosphate of lime. Directly under this bed lies a second stratum of phosphate rock from 2 to 4 feet in thickness, which closely resembles that just described. It is, however, less oolitic and contains appreciably less P_2O_5 . The average grade of this second stratum is from 30 to 40 per cent bone phosphate of lime and therefore during mining operations it was separated from the upper stratum and thrown away as unmarketable rock.

In the following table (Table XV) are given the analyses and descriptions of the successive strata of phosphate rock sampled by the senior author at two different places.

TABLE XV

ANALYSES AND DESCRIPTION OF PHOSPHATE STRATA FROM TWO DIFFERENT LOCALITIES IN ARKANSAS

Sample No.	Location	Thickness of Strata	Description	Analyses	
				P_2O_5	$Ca_2-(PO_4)_2$
..	"Phosphate," 12 miles northwest of Batesville	2' 6"	Ferruginous Limestone (roof)	Trace	..
93	"	6"	Green shale	5.82	12.72
89	"	4' 0"	Hard, gray, nodular	28.85	63.05
91	"	2' 0"	Hard, gray, less nodular	14.16	30.94
97	1 1/4 miles north of "Phosphate"	1' 6"	Ferruginous phosphate	19.60	42.94
94	"	6"	Thin bedded slate (not sampled)
96	"	3' 0"	Hard gray oolitic phosphate	22.96	50.18
95	"	1' 0"	Hard, gray, oolitic phosphate	10.01	21.87
98	"	Undetermined	Ferruginous shale	7.53	16.45

The Arkansas phosphate was mined in the same way as the blue rock phosphate of Tennessee, by first stripping around the face of the hill till the overburden became too heavy to be profitably removed, and then running drifts into the hill's side. As these tunnels are driven deeper into the hills comparatively little timbering is required since the stratum of unweathered limestone and shale overlying the phosphate beds form a fairly substantial roof.

Mining operations ceased in the Arkansas phosphate fields in 1912.

RESERVE SUPPLY OF PHOSPHATE ROCK IN THE UNITED STATES.

Any estimate of the reserve supply of high grade phosphate rock in the United States must be at best only an approximation, because, as previously pointed out, the limits and extent of many of the phosphate deposits can be determined only by careful and detailed prospecting. In the two accompanying tables (Tables XVI and XVII), however, one compiled by the senior author in 1913 and the other by W. C. Phalen in 1915, estimates of the amount of phosphate rock available in the various fields of this country are given.⁸⁷ Several million tons of phosphate have been mined since these estimates were made and therefore the tables are brought up to date by deducting the amount produced during this 11 to 13 year period. No deduction is made for the Western phosphates, since the tonnage mined in this period is more than offset by further discovery.

Since the annual output of high-grade phosphate rock from our Eastern deposits is normally about 3,000,000 tons, these more accessible fields may be exhausted within a hundred years even should there be no greater consumption than at present. But if our agricultural production is to continue its steady healthy growth, we must expect a far greater demand for phosphatic fertilizers than now exists. Under the present system of mining and preparing phosphates for the market it is not inconceivable that many deposits will be exhausted within the next 50 years, for the demand for high-grade rock carrying from 68 to 75 per cent or more of bone phosphate of lime is such that lower grade material receives little consideration.

The figures given in Table XVI show that the bulk of our phosphate material is of relatively low grade, much of which is being or will be wasted because of its close association with the higher grade rock and the apparent necessity of discarding finely divided phosphate in the mechanical separation of such impurities as clay and sand.

In Table XVIII is given the phosphate content of run-of-mine phosphate from various sources, the composition of the lower grade strata so intimately associated with higher grade phosphate rock and the waste material which is discharged in preparing a higher grade marketable product.

A study of these tables makes it appear evident that unless methods are devised and adopted whereby a fuller utilization of our phosphate resources is effected, the exhaustion of our Eastern reserves is a matter of only a century at best. While the deposits of high grade

⁸⁷ Reserve Supply of Phosphate Rock in the United States, J. Ind. Eng. Chem., 1914, Vol. 6, p. 464, and Phosphate Rock in 1915, Mineral Resources, U. S. Geological Survey, 1916, Part II, pp. 227-244

phosphate rock in the West might continue to supply our needs for several more centuries the long haul required to bring this rock to the Eastern market would add greatly to the cost of the fertilizer.

Fortunately there is evidence that new processes are being developed whereby lower grade materials can be successfully employed as well as the high grade phosphates in producing soluble or available phosphoric acid. The advances which have been made along these lines are discussed in another chapter.

TABLE XVI
RESERVE SUPPLIES OF HIGH-GRADE AND LOW-GRADE PHOSPHATES IN THE
UNITED STATES

	Tons
Utah, Idaho, Wyoming and Montana:	
High-grade	2,500,000,565
High-grade equivalent of all grades.....	7,500,000,000
Florida:	
High-grade equivalent of all grades.....	336,841,936
High-grade equivalent of wash heaps.....	20,000,000
Tennessee:	
High-grade equivalent of all grades.....	111,108,302
South Carolina:	
High-grade equivalent of all grades.....	9,471,752
Arkansas:	
High-grade equivalent of all grades.....	20,000,000
Kentucky:	
High-grade equivalent of all grades.....	500,000
	10,497,912,555

TABLE XVII
ESTIMATED QUANTITY OF PHOSPHATE ROCK AVAILABLE IN THE UNITED STATES
(U. S. GEOLOGICAL SURVEY)

	Long Tons
Eastern States:	
Florida	214,584,714
Tennessee	85,357,825
South Carolina	8,771,464
Kentucky	1,000,000
Arkansas	20,000,000
Total	329,714,003
Western States:	
Utah, Idaho, Wyoming and Montana.....	5,367,082,000
Grand total	5,696,796,003

TABLE XVIII

PHOSPHORIC ACID CONTENT OF RUN-OF-MINE, LOW-GRADE AND VARIOUS WASTE PHOSPHATES WHICH CANNOT BE USED IN MANUFACTURE OF ACID PHOSPHATE

Materials	Location	Thickness of Bed or Stratum, Feet	Description	Analyses	
				P ₂ O ₅ Per Cent	Ca ₃ (PO ₄) ₂ Per Cent
Run of mine (hard rock)	Newberry, Fla.	Not det.	Cream-colored material containing clay and lump rock	30.69	67.00
Waste from washer	Newberry, Fla.	Not det.	Sand, clay and soft phosphate	12.14	26.59
Waste from washer	Anthony, Fla.	Not det.	Sand, clay, finely divided phosphate	12.70	28.21
Material from picking belt	Dunnellon, Fla.	Clay balls containing phosphate, lime, rock, etc	11.60	25.40
Run of mine (pebble)	Mulberry, Fla.	20	Pebble phosphate, sand, clay and soft phosphate	21.52	47.02
Waste from washer	Mulberry, Fla.	Not det.	Sand and finely divided phosphate	14.57	31.83
Run of mine	Bartow, Fla.	Not det.	White, soft claylike	23.61	51.59
Run of mine	Ridley, Tenn.	6 to 10	Brown plates, finely divided phosphate, clay, and sand	25.84	56.70
Run of mine	Mt. Pleasant, Tenn.	5 to 7	Brown plates, finely divided phosphate, clay, and sand	26.44	58.00
Waste from washer	Mt. Pleasant, Tenn.	10 to 15	Finely divided phosphate, sand and clay	14.21	31.20
Run of mine (best grade)	Wales, Tenn.	10 to 20	Brown disintegrated phosphate, sand and clay	23.85	52.25
Run of mine (medium grade)	Wales, Tenn.	10 to 20	Brown disintegrated phosphate, sand and clay	20.00	43.80
Run of mine (low grade)	Wales, Tenn.	10 to 20	Brown disintegrated phosphate, sand and clay	11.23	24.60
Phosphate shale	Georgetown, Idaho	42	Brown calcareous phosphatic shales	23.6	51.60
Bedded phosphate	Near Batesville, Ark.	6	Hard, grayish brown oolitic	24.8	54.20
Bedded phosphate	Near Batesville, Ark.	2	Hard grayish brown oolitic	14.2	31.00
Run of mine	Woodford Co., Ky.	6 ³ / ₄	Thin bedded phosphate mixed with sand and clay	22.85	50.00
Run of mine	Jessamine Co., Ky.	8 ¹ / ₄	Soft, dark brown easily disintegrated	23.70	51.80

Chapter 3.

Phosphates of Foreign Countries.

NORTHERN AFRICA.

While the annular production of phosphate rock in the United States still exceeds that of any other single country, the development of the phosphate deposits in Northern Africa has now reached such huge proportions that the combined output of Tunis, Algeria, Egypt, and Morocco is actually greater than that of the United States. The African phosphates therefore have become a very serious competitor of the American product in the European market.

When it is considered that the phosphates of Tunis and Egypt were either undiscovered or undeveloped until 1897 and that development work in Morocco was not begun until 1917, the expansion of the phosphate industry in these countries has proceeded with surprising rapidity.

From a production (in Algeria) of 104,603 tons in 1895 the combined annual output of the four countries mentioned above has grown steadily until in 1924 it reached 3,000,000 tons.

Almost the entire output of phosphate rock from Northern Africa (with the exception of a portion of that mined in Egypt) is shipped to Europe where the countries are so thickly populated that intensive systems of agriculture must necessarily be employed. The European farmer realizes that one of the most effective ways (within his control) to increase crop yields is by the liberal and regular use of phosphatic fertilizers.

Although the development of the Northern Africa deposits has adversely affected our export trade, it is nevertheless fortunate that Europe is no longer entirely dependent on America for its supply of phosphate rock. The use of phosphate fertilizers in the United States is growing and must continue to grow as our so-called virgin lands become depleted in fertility. So no matter how vast our phosphate resources may appear to be we will need them to insure an agricultural output adequate to meet the demands of our ever increasing population.

Tunisian Phosphate.

Next to the United States Tunis is the largest phosphate producing country in the world its annual output having now reached 2,000,000

metric tons. While the phosphate area of Tunis can be traced for hundreds of miles and represents a reserve supply estimated at several hundred million tons, the most important deposits where commercial development has taken place is in the vicinity of Gafsa close to the Algerian border. These mines are connected by rail to the ports of Sfax and Sousse which represents a haul of approximately 150 miles to transport the rock to the sea coast.

The deposits are of Eocene age and occur in beds several feet in thickness but only those containing over 50 per cent of bone phosphate of lime, and within close proximity to the railroad are at present being exploited.

These deposits as well as their development have been frequently described in Government publications and the scientific press,¹ so only brief descriptions are included here

According to Stone² the phosphate mines at Gafsa contain four principal beds and by mixing the material from two beds 10 feet and 6 feet in thickness respectively a product is obtained which averages 60 per cent bone phosphate of lime.

The deposits of phosphate in Tunis are controlled by French capital and the "Compagnie de Gafsa" is the largest single producer of phosphate rock in the world. Other companies operating in Tunis are "Compagnie de Phosphates Tunisiennes," "Compagnie de Phosphates du Dyr," and "Compagnie de Saint Gobain."

Much of the mining in the Gafsa region is conducted by tunneling into the phosphate strata and digging the rock out in the manner employed in mining seams of coal. The phosphate rock requires no washing process like that employed in Florida and Tennessee in order to prepare a marketable product.

The following description of mining, handling, drying, and shipping the phosphate from the Gafsa mines is given in a translation by R. W. Stone³ of a paper published by Émile Morinaud in "Les Annales Coloniales" in 1921.

¹ King, P. Phosphate Mining in Tunisia, Trans Inst Min Eng, 1913-1914, p. 456, Keppen, A. de, Industrie Minérale de la Tunisie, Comité Central des Houillères de France, Paris, 1914, Phosphate Industry of Tunis, American Fertilizer, p. 114, Sept. 27 (1919); Compagnie des Phosphates de Gafsa, Echo des Mines et de la Metallurgie, p. 353, June 15, 1919; Geissel, H. L., Phosphate in Tunis, Eng and Min Jour, p. 861, May 21, 1921, Société des Phosphates Tunisiennes, Echo des Mines et de la Metallurgie, p. 30, July 10, 1924, Compagnie des Phosphates du Maroc et la Main d'œuvre, Echo des Mines et de la Metallurgie, p. 334, July 20 (1925), Mineral Resources of the British Empire and Foreign Countries, Phosphates, p. 58 (1921), Morinaud, E., Phosphate in Algeria and Tunis, Les Annales Coloniales, Paris, Feb. (1921).

² Phosphate Rock in 1919, Mineral Resources, part 2, p. 221, U. S. Geol. Survey (1921).

³ Phosphate in Algeria and Tunis, Amer. Fertilizer, p. 62, Dec. 31, 1922.

"The equipment of the Gafsa company is suited to the exceptional productive capacity of the mines. At Metlaoui, mining is done on two beds of a thickness of 2.5 meters and of 1.8 meters. The galleries extend into the Louisif, Jacha and Metlaoui plateau terrace. The total of the subterranean works occupies an area of 4.5 kilometers long and about 500 meters wide. About 800,000 tons is mined each year.

"The phosphate is transported by mine cars in trains drawn by electric locomotives to chutes which load the railroad cars. These latter go in full trains to Metlaoui, where the phosphate is dried partly by exposing and working in the sun, and partly by numerous and powerful drying furnaces each with a capacity of 15 to 20 tons an hour. The dry phosphate is stored in great covered sheds. It is either kept in stock or loaded directly from the drier and sent to Sfax in full trains.

"At Redeyef the mine produces an average of 400,000 tons a year. The equipment is less complete than at Metlaoui, for part of the phosphate mined at Redeyef is dried at Metlaoui. The mine cars at Redeyef are drawn by gas locomotives. The motive power is produced by two central gas stations developing about 1,000 horse power at Metlaoui and 500 horse power at Redeyef. The phosphate brought from the mine to the Philippe-Thomas station is loaded into trains with a capacity from 1,000 to 1,500 tons. The railroad, which is equipped in the most modern way, transports the phosphate to Sfax; it possesses in particular 10-wheel engines which are the most powerful engines used on 1-meter roads. These engines weigh about 56 tons.

"The same railway serves, between Metlaoui and Sfax, several centers of population and two other mines which bring to it a very interesting commercial traffic which is growing daily. At Sfax the loading equipment is remarkable for its size, for the system of handling used and for the enormous capacity of the apparatus for loading ships. The company easily loads 6,000 tons a day. The light and power station (500 h. p.) is situated on the quay. Transportation of phosphate to different points in the enormous sheds is done by rubber belt conveyors which serve also to lift the material again and take it to the loading apparatus, each one of which is capable of putting on ship 250 to 300 tons an hour. At Sousse a similar equipment permits the loading of 250,000 tons for shipment from that port."

Algerian Phosphate.

The phosphates of Algeria have been described in a number of government publications as well as in numerous articles published in the scientific press,⁴ so in the present work the writers have confined

⁴ Algerian Phosphates, Min. Jour., Mar. 6, 1920; Algerian Phosphates, Amer. Fertilizer, p. 67, Aug. 16, 1919; Frost, A. C., The Algerian Phosphate Industry,

themselves to a brief description and discussion of these deposits.

The Algerian phosphates were the first to be developed in Northern Africa, and since 1895 the production from these fields has gradually but steadily increased.⁵

These phosphates occur in sedimentary beds of Eocene age and are of the same general character and age as those of Tunis. In fact the Algerian and Tunisian phosphates are practically identical since the border line between these two countries cuts through the phosphate region.

Only a portion of the phosphate area of Algeria has been developed, the most important mines at present being located near the towns of Setif and Tébessa in the Department of Constantine Eastern Algeria. Here the phosphate occurs in a basin shaped deposit composed of five separate beds, three of which are considered worth mining. These workable beds vary from $1\frac{3}{4}$ to 9 feet in thickness and are mined chiefly by open cuts; only where the overburden exceeds 24 feet is tunneling practiced. From the mines the phosphate is brought by cable or tram cars to central plants where it is crushed and sorted. No washing process is required in preparing this rock for the market, so after grinding (and sometimes drying) the phosphate is loaded into railway cars and transported to the Mediterranean ports of Bone, Bougie, and Algiers for shipment to European countries.

Sulfuric acid factories at Oran Maison C'orrée (near Algiers) and at Bone make it possible to produce as high as 86,000 tons of super-phosphate per annum, which is more than the colony's requirements and leaves a balance for export.

The marketed grades of Algerian phosphate range from 58 to 68 per cent bone phosphate of lime.

The largest producer of phosphate rock in Algeria is the "Compagnie des Phosphates de Constantine." This company controls some of the highest grade deposits in the phosphate area and has installed the latest and most up-to-date equipment for mining, handling, sorting, drying, and loading the phosphate. Other companies operating in Algeria are the "Compagnie des Phosphates de Toqueville" and the "Compagnie Centrale des Phosphates de Bordj Redir."

In addition to the developed phosphate deposits of Algeria there

Commerce Reports, p. 788, Feb. 9, 1920; Elkington, David C., Algerian Phosphate Mining Industry, Commerce Reports, p. 453, Aug. 14, 1922, Elkington, D. C., Prospective Algerian Phosphate Developments, Commerce Reports, p. 350, Nov. 10, 1924; Morinaud, E., Phosphate in Algeria and Tunis, Les Annales Coloniales, Paris, Feb., 1921, translated by R. W. Stone in American Fertilizer Handbook, 1921 Edition; Fabrega, D. P., The Phosphate Deposits of Northern Africa, Min. Jour., Feb. 8, 1919.

⁵ With the exception of the war period and the two years immediately following (1918 and 1919).

are a number of areas which have not yet been exploited because of lack of transportation facilities. The most important of these are Djebel Onk and Maadids.

The former deposits are very large and should in time prove highly productive. The beds are said to be from 30 to 60 meters in thickness and are variously estimated to contain from 300,000,000 to 1,000,000,000 tons of phosphate rock with an average content of 66 per cent bone phosphate of lime^o. These deposits, however, are located from 50 to 60 miles south of the terminus of the nearest railroad at Tebessa and hence their development at present is commercially impracticable.

The latest official statistics on the production of phosphates in Algeria are those for 1924, when 583,234 tons were produced

Moroccan Phosphate.

The phosphate deposits of Morocco also belong to the Tertiary period and occur in strata of upper and lower Eocene. The first deposit recognized was that of El Boroudj, which was discovered in 1912, but it was not until 1921 that any amount of development work was done. In that year only 6981 tons were marketed from the Moroccan fields, but with the completion of a standard gauge railroad the production has grown by leaps and bounds and in 1925 reached the remarkable figure of 720,000 tons.

The deposits of El Boroudj are in the central part of the northwest coastal region from 80 to 90 miles south-southeast of Casa Blanca, a seaport on the Atlantic coast. The phosphate region stretches from east to west for a distance of 60 miles from Oued-Zem to Dar-Chafai.

^oPhalen, W. C., The Conservation of Phosphate Rock, Trans. of Amer. Inst. of Min. Engrs., p. 1931 (1917), Min. Ind. of British Empire, Phosphates, p. 57, 1921.

¹For details concerning the geology, development and nature of the Moroccan phosphates the reader is referred to the following publications:

Jumeau, P., Phosphate Deposits in Morocco, Amer. Fert., Vol. 53, p. 142, Oct. 9, 1920, The Newly Discovered Phosphate in Africa, Amer. Fert., Vol. 53, p. 90, May 22, 1920, Martin, J. C., Phosphate Rock Deposits in Morocco, U. S. Geological Survey Press Bulletin, Sept., 1920, The Moroccan Phosphate Beds, Amer. Fert., Vol. 54, p. 106, June 4, 1921, The Importance of Moroccan Deposits, Amer. Fert., Vol. 54, p. 81, June 18, 1921, Development of Moroccan Phosphates, Amer. Fert., Vol. 54, p. 92, Oct. 8, 1921, Lloyd, S. L., Moroccan Phosphate Deposits, Eng. & Min. Jour. Press, Vol. 113, p. 556, April 8, 1922; Phosphate Beds of Morocco, Mining Jour., p. 126, Feb. 17, 1923, Moroccan Phosphate Offered in European Countries, Chem. & Met. Eng., Oct. 6, 1924, Russell, H. E., Notes on the Production of Phosphates in Morocco, Special Circular 105, Bureau of Foreign and Domestic Commerce, July 13th, 1925; Rapid Advance in Phosphate Output of Morocco, Chem. & Met. Eng., Feb. 9, 1925, Les Phosphates du Maroc et la Main d'œuvre, Echo des Mines et de la Metallurgie, p. 409, Sept. 10, 1925, Mansfield, G. R., Phosphate Rock in 1924, Bureau of Mines, Mineral Resources of the U. S., part II, p. 101, 1925.

Its northern limit approaches Guisser and its southern boundary is the El Boroudj cliff overlooking the plain. This area is about 400,000 acres in extent and is variously estimated to contain from several million to one billion tons of relatively high grade phosphate, much of which lies near the surface and is a gray fragile rock of such a character as to require little or no treatment to prepare it for the market.

Since the discovery of the first deposit of phosphate, other beds of great value and extent have been found which bid fair to make Morocco an even more important phosphate producing country than Algeria and Tunis.

It was thought at first that the reports concerning the grade and extent of the Moroccan phosphates were highly exaggerated, and in 1920 Jumeau⁸ published a number of analyses showing that much of the rock was no richer than that of Algeria and Tunis. Later investigations, however, have proven that large tonnages are available which contain 70 per cent and more of phosphate of lime, and certain samples run considerably higher. Such phosphate compares very favorably with that from the Florida pebble fields and its appearance on the market has had a depressing effect on the American export trade.

The following brief description of the equipment for and method of handling the Moroccan phosphate is taken from the report of H. Earle Russell,⁹ American Consul at Casa Blanca.

"At Boujniba there has been for some time a very up-to-date plant for the crushing and drying of phosphate, and recently an equally modern plant for storing and loading has been installed there. The accumulators are constructed of reinforced concrete 120 meters long, 60 meters wide, on trusses of 20 meters, and have a capacity of 60,000 metric tons. The phosphate is brought from the crushing and drying section of the plant to the upper part of the storage bins and distributed over the entire surface of a belt. Six series of hoppers allow the loading of the cars in rapid succession, so that a train of 300 tons can be loaded in 2 minutes by each series. Nearly all of the phosphate is now brought to Casa Blanca by the normal gauge railway line, a distance of about 90 miles. From a point near Kourigha to the sea there is a gentle incline, which will permit cheap transportation when the line is electrified. The warehouses at Roches-Noires, a suburb of Casa Blanca, are no longer used and the loaded cars are run directly to the port and unloaded automatically, the contents being carried by belts to the top of the elevator, whence they are discharged into the holds of the vessels lying alongside the quay. The present elevator can load

⁸ Phosphate Deposits in Morocco, Amer Fert, Vol 53, p 142, Oct 9, 1920.

⁹ Notes on the Production of Phosphates in Morocco, Special Circular 105, Bureau of Foreign and Domestic Commerce, July 13, 1925.

vessels at the rate of 350 metric tons per hour, or more than double the present necessary rate.

Egyptian Phosphates.¹⁰

Phosphate rock occurs in many localities in Egypt, but the only deposits which have any commercial importance at present are those along the banks of the Nile River (in the Sabaia District) and near the coast of the Red Sea.

While the Egyptian phosphates are somewhat similar in character to those of Tunis and Algeria they belong to an earlier geologic period, geologists generally agreeing that they are of Cretaceous age.

The rock was first discovered in 1897 near the village of Esna on the east bank of the Nile River and subsequently found to cover a considerable area on both sides of this stream. These deposits, while still being mined and shipped from the port of Alexandria by an Italian company, are not on the whole as important and as high grade as those near the coast of the Red Sea in the districts of Quosseir and Safaja. The Egyptian phosphate strata vary greatly in thickness, appearance and grade, not only from place to place but even within small areas. As a whole they are light in color and sufficiently friable to be readily crushed. The marketable grades range from 58 to 68 per cent bone phosphate of lime with an iron and alumina content of from 1 to 3 per cent.

The deposits near the Red Sea are being developed at Safaja (18 miles from the coast) by an English company, and at Quosseir and El Sabaia by an Italian company which exports most of the product to Italy.

The English company (at Safaja) transports its rock to the coast by means of an electric railroad, and from there ships most of it through the Suez Canal to Japan. From a production of 700 tons in 1908 the output of Egyptian phosphate increased steadily up to 1913, when 102,771 tons were produced. During the war period, however, the annual output from these fields decreased greatly, and while there was a marked recovery in 1920 and 1921 the subsequent development

¹⁰ For descriptions of the location, geology and development of the Egyptian phosphates the reader is referred to the following publications: Barron, Hume, Beadnell and Lucas, *A Report on the Phosphate Deposits of Egypt*, Egyptian Geological Survey, Cairo, Egypt (1900); Ball, J., *The Phosphate Deposits of Egypt*, Survey Dept. Paper No. 30 (1913); Ball, J., *Topography and Geology of the Phosphate District of Safaja*, Survey Dept. Paper No. 29 (1913); Cortese, E., *Phosphate in Egypt*, Trans. Amer. Inst. of Min. Engrs., Vol. 59, p. 112 (1918); *Egyptian Phosphate*, Chap. 5, p. 14, Dept. of Mines and Quarries, Cairo, Egypt (1922); *The Mineral Resources of the British Empire, Phosphates*, pp. 30-31 (1921); DuBois, C., *Phosphate Along Red Sea Coast of Egypt*, Commerce Reports, Mar. 5, 1923.

of the higher grade deposits in Morocco has again had a somewhat depressing effect on the Egyptian phosphate industry.

The phosphate deposits near the Red Sea are mined in a manner similar to coal seams, the pillar and stall system being employed at Quosseir and the long wall system at Safaja.

PHOSPHATES OF THE PACIFIC AND INDIAN OCEANS.¹¹

The highest grade phosphates known to the world today occur on certain small islands in the Pacific and Indian Oceans. The origin of these phosphates is generally conceded to be guano deposited by myriads of birds which fed on the marine life abounding in these regions and lived, bred, and died on these islands. Many of these birds are now extinct and the guano has been leached and its soluble phosphate content fixed by the underlying coral formations of which these islands are largely composed. The resultant phosphates have a content of from 80 to 88 per cent calcium phosphate and are being extensively developed by English, French and Japanese interests.

Nauru or Pleasant Island.

This island is only 26 miles south of the equator and lies in longitude 165 degrees 55' east and is about 2200 miles from Sydney, Australia. It is an isolated island not belonging to any group and the nearest land is Ocean Island about 200 miles to the southeast. Nauru has a total area of about 12 square miles, most of which is phosphate bearing. A strip of land along the coast from 100 yards to a quarter of a mile in width is relatively level, but beyond this level belt the land rises to a height of over 200 feet. This elevated portion of the island consists almost entirely of phosphate rock and coral pinnacles.

The phosphate was recognized as such about the year 1900 and exploitation began in 1906.

The phosphate, which is a surface deposit with little or no overburden, is almost pure white. It is mined by pick and shovel and has

¹¹ For descriptions of the Pacific and Indian Ocean phosphate deposits the reader is referred to Elschner, C., *The Island of Nauru, American Fertilizer*, p. 23, Dec. 13, 1913; Winslow, A. A., *Phosphate Deposits in the South Pacific*, Commerce Reports, Sept. 15, 1918; *Pacific Island Phosphate Deposits*, Eng. and Min. Jour., Feb. 7, 1920; *Nauru Phosphates*, Amer. Fert., p. 89, Feb. 11, 1922; *The Nauru Phosphates*, Amer. Fert., p. 33, April 22, 1922; *The Phosphate Deposits of the Pacific*, Amer. Fert., Vol. 58, p. 25, Feb. 10, 1923; *Nauru and Ocean Island Phosphate*, Canadian, Chem. & Met., p. 105, April, 1923; *Nauru and Ocean Island Phosphates*, Amer. Fert., Vol. 58, p. 68, Nov. 3, 1923; *The Mineral Industry of the British Empire*, Phosphates, p. 49, 1921; Mansfield, G. R., *Phosphate Rock in 1924*, p. 107, *Mineral Resources*, part II, U. S. Bureau of Mines, 1925.

to be dug frequently from around pinnacles of coral which often rise to a height of 30 feet from the lime stone bed rock. The excavated material is transported to tram cars by cable hoists and subsequently crushed and calcined in large rotary driers.

On account of lack of harbors the loading of the Nauru phosphate at first presented serious difficulties, but modern cantilever jetties have been built which reach from 70 to 80 feet beyond the outer edge of the coral reef surrounding the island. From these jetties the rock is loaded into lighters which convey the phosphate to the ships which are moored as close to shore as possible. Improvements in the loading system are now contemplated which will permit vessels to be loaded directly from the shore. This will not only increase the output but will render the industry more nearly independent of adverse weather conditions. The reserve supply of high grade rock on Nauru Island is estimated at 100,000,000 tons.

Before the war the island of Nauru was controlled by Germany, but it has now passed into the hands of Great Britain and the phosphate is being exploited for the benefit of agriculture in the United Kingdom, Australia and New Zealand.

Ocean Island.

Ocean Island is one of the Gilbert group. It is only about one-third the size of the island of Nauru but the phosphate occurs under the same conditions, is of similar origin and of an equally high grade.

Phosphate rock was discovered on this island at a somewhat earlier date than that on Nauru and exploitation began in 1900. The best deposits are found on the central table land where the phosphate beds extend to a depth of 50 feet.

The phosphate is mined by first removing a light overburden and then breaking out the rock with pick and shovel. The excavated material is then run by a gravity tramway to driers and storage bins from which it is loaded into vessels in the same manner as the Nauru phosphate.

The annual output from Ocean Island has ranged from 50,000 to over 200,000 tons of 85 per cent phosphate rock for the past 15 years. It is estimated that there is still a reserve supply of 50,000,000 tons of high grade rock on the island. The deposits are also controlled by Great Britain.

Christmas Island.

This island, which is also under the control of Great Britain, is situated in the Indian Ocean, about 190 miles southwest of Java. The

phosphate deposits are similar in origin and appearance to those of Ocean and Nauru islands but slightly lower in grade, averaging about 80 per cent bone phosphate of lime. The annual output from this island reached a maximum of about 300,000 tons in 1912. It is doubtful if such a production will ever be attained again.

Australia.

Phosphate deposits are known to occur in a number of widely scattered localities in Australia,¹² but relatively few of them are of much commercial importance. The most productive area is in S. Australia, where the phosphate occurs associated with Cambrian and pre-Cambrian lime stones.

The phosphate is usually mined by open quarry, but in some instances by the pillar and stall system. The grade of the rock varies all the way from below 50 per cent to above 60 per cent bone phosphate of lime. That which is marketed averages about 60 per cent. Australia has a total annual production of about 10,000 tons, most of that consumed being imported from Ocean, Nauru, and Christmas Islands.

The Island of Makatea.

The small island of Makatea is one of the Society group about 120 miles north of Tahiti. It has an area of only 1200 acres, but much of it contains phosphate rock similar in character and grade to that found on Ocean and Nauru Islands.

The phosphate which has an average content of 80 per cent of tricalcium phosphate is mined by pick and shovel and hauled in train cars to a crushing, drying and storage plant, from whence it is loaded into lighters by means of two piers about 300 meters in length and transported to vessels which are moored off shore. The annual output from this island has ranged from 31,000 to 80,000 tons during the past 15 years, but it is estimated that there still remains about 10,000,000 tons of high grade rock.

¹² Report of the Dept. of Mines, Sydney, New South Wales (Annual); Carne, J. F., Annual Report, Dept. of Mines, N. S. W., for 1914, pp. 191-194; Carne, J. F., and Andrews, P. C., Annual Report, Dept. of Mines, N. S. W., for 1916, pp. 202-204; Morrison, M., Phosphate Rock, Canowinda, Annual Report, Dept. of Mines, N. S. W., for 1917, p. 169; Skeats, W. E., and Teale, F. D., A New Phosphate Deposit in the Howqua District, Proc. Austr. Inst. Min. Eng., New Series, No. 32, pp. 155-175 (1918); Ball, L. C., Phosphates at Gore, Queens, Govt. Min. Jour., Brisbane, Vol. 18, p. 443 (1917); Woodward, H. P., The Phosphatic Deposits of Western Australia, W. Austr., Geol. Survey, Perth, Bull. 74, Misc. Reports, Ser. 5, No. 61, pp. 9-28; Jack, R. L., The Phosphate Deposits of South Australia, S. Austr. Dept. of Mines, Adelaide, Geol. Survey, Bull. 7, p. 136 (1919); Frew, J., Phosphates, S. A. Min. & Eng. Jour., Dec. 5 and 19 (1925).

Angaur Island.

Angaur Island is one of the Pellew group, about 800 miles east of the southern end of the Philippine Islands. Before the war this island belonged to Germany, but by the terms of the peace treaty has now passed into the hands of the Japanese, who are exploiting the phosphate deposits for the benefit of their own agricultural interests. The approximate annual production is about 30,000 tons. The rock is of an excellent grade, averaging 80 per cent or more of tricalcium phosphate, and is readily and cheaply mined. It is estimated that this island still contains from 2,000,000 to 3,000,000 tons of high grade phosphate.

PHOSPHATES OF EUROPE.

At one time Belgium, England, and France produced a considerable tonnage of low grade phosphate rock which was depended upon to meet the agricultural demands of those countries for soluble phosphate fertilizers.

While these phosphate deposits are not yet entirely exhausted the discovery of the vast fields of higher grade and more cheaply mined phosphates in the United States soon caused mining operations in these countries to decline, and since the development of the immense phosphate deposits of Northern Africa the exploitation of these European phosphate deposits has almost ceased.

With the exception of Belgium, however, these countries own or control extensive and valuable phosphate areas in Africa and on certain islands in the Pacific and Indian Oceans.

Belgium.

The principal phosphate region in Belgium is situated at Ciply and Mesvin, near Mons, which was part of the Flanders battle area during the late war.¹³

The Belgian phosphates occur either as nodules imbedded in a matrix of clay or as beds of phosphatic chalk in Tertiary and Cretaceous strata. The grade of the rock now available averages only from 40 to 45 per cent tricalcium phosphate and contains such a large proportion of acid consuming impurities that it is uneconomical to use it alone for the manufacture of superphosphate. Accordingly the small tonnage which is mined is mixed with the richer phosphates from other sources in order to give available or water soluble phosphates of marketable grade.

¹³ *Statistique des Industries Extractives et Metallurgiques en Belgique* (Annual); *Mineral Resources of the British Empire, Phosphates*, p. 51 (1921).

The annual production of phosphate rock in Belgium is now approximately 50,000 tons.

England.

Phosphates in the form of coprolites occur over widely scattered areas in the British Isles,¹⁴ but the rock is of such a low grade that it now has but little commercial significance.

The most productive deposits have been those in the Cambridge upper Green sand, where the beds consist of dark brown or black nodules from 8 to 12 inches thick and from a bed (12 to 18 inches thick) of similar material in Suffolk.

The average grade of the English coprolites is below 50 per cent tricalcium phosphate and the rock contains such a high percentage of iron that it is impracticable to use it for the manufacture of acid phosphate unless it is blended with a large proportion of high grade phosphate from other sources.

As in the case of Belgium the exploitation of these coprolite deposits is no longer profitable, and while mining operations were revived for a short period during the war because of the difficulty of importing from foreign sources, production has again practically ceased.

France.

Low grade phosphates occur in the Departments of Aisne, Ardennes, Meuse, Oise, Pas de Calais and Somme. The rock is of Cretaceous age and occurs in the form of phosphatic chalk and as narrow bands from 2 to 10 inches thick in Cretaceous Green sand.

The rock ranges in grade from 45 to 65 per cent tricalcium phosphate and while at one time of considerable importance from an agricultural standpoint is now unable to compete with the phosphates of the United States and Northern Africa. Mining operations are still conducted, however, on a limited scale the rock being mixed with higher grade phosphates from other sources and manufactured into acid phosphate.

During the war practically all of the phosphate area of France was in German hands, so the nation had to depend entirely upon the rock shipped in from Africa and the United States for its supplies of superphosphate.

Germany.

It seems rather strange that a nation which consumes such a large tonnage of phosphate fertilizers should not have discovered any phos-

¹⁴ Mineral Resources of the British Empire, Phosphates, p. 23 (1921).

phate deposits of commercial importance on its own domain until very recently.

Next to our own country, Germany has been the greatest market for Florida phosphate and prior to the war her annual consumption of phosphate rock (all of which was imported) amounted to one million tons.

No deposits of phosphate of economic value were known in Germany until 1918, and during the war she had to depend almost entirely upon her output of basic slag to meet the demands of agriculture. Even with the increased production of this material, caused by the expansion of the steel industry, there was a very grave shortage of phosphatic fertilizer and every effort was made to discover workable beds of phosphate rock within the country.

Finally in 1918 a deposit was found in the vicinity of Nuremberg, Bavaria. This bed is said to attain a thickness of 10 feet in many places and certain samples have been found which contain 80 per cent of tricalcium phosphate. The deposit as a whole, however, is of a low grade and is estimated to average only 35 per cent tricalcium phosphate. It hardly seems likely, therefore, that such phosphate can now be profitably mined in competition with the higher grade deposits of other countries.

Russia.

While the phosphates of Russia have only been exploited to a limited extent, deposits of considerable magnitude and importance occur in Jurassic and Cretaceous rocks both in Northern and Southern Russia.¹⁵

Only those in the south in the Governments of Podolia and Bessarabia, however, have so far been exploited to any extent. Before the war these were mined by underground methods and the rock which is said to average 75 per cent tricalcium phosphate was shipped to Poland and manufactured into superphosphate.

A. A. Michno¹⁶ gives the following analyses of the Podolian phosphorite.

¹⁵ Kaunhowen, F., *Über Russische Phosphorite*, *Zeits. für prakt. Geol.*, Vol. 27, p. 71 and p. 89 (1919); *Mineral Resources of the British Empire*, Phosphates, 1, p. 55 (1921); *Russian Phosphate Industry Revives*, *Amer. Fert.*, p. 82, April 8, 1922; Dougherty, W. T., *Possibility of Russian Phosphates for Germany*, *Commerce Reports*, Aug. 6, 1923; Tokarski, J., *Phosphorite in Podolia*, *Przemysl. Chem.*, Vol. 7, p. 57 (1923); Samoilov, I., *Phosphorite Deposits of Russia*, *Chem. zentralb.* Bd. 3, p. 732 (1923); *Russian Phosphorites*, *Amer. Fert.*, p. 59, Aug. 9, 1924; *The Phosphate Industry in Russia*, *Amer. Fert.*, p. 66, May 30 (1925); Mansfield, G. R., *Phosphate Rock in 1924*, *Mineral Resources*, Part 11, U. S. Bureau of Mines (1925).

¹⁶ *Russian Phosphorites*, *Amer. Fert.*, p. 59, Aug. 9, 1924.

	Per Cent
Silica	5.05
Al ₂ O ₃	1.12
Fe ₂ O ₃	1.90
CaO	49.50
MgO	.37
P ₂ O ₅	38.38
SO ₃	0.42
CO ₂	0.31
K ₂ O & Na O	0.07
Loss on ignition	1.66
<hr/>	
Total	98.78

It is doubtful, however, if the above analysis is typical of these deposits, for such rock is exceptionally high grade. The deposits in Southern Russia have been estimated to contain as much as 80,000,000 tons of phosphate rock.

The phosphates in Northern Russia in the Governments of Vladimir, Krostom, Viatka and Yaroslav have not yet been exploited, but it is said that careful geologic surveys have shown them to be of considerable extent.

In addition to the two main phosphate districts, deposits of Cretaceous phosphate rock occur on the central part of European Russia near Moscow, which are said to be excellently located for commercial development. So far these deposits have been worked only to a very limited extent, but as conditions become more stable it appears likely that Russian phosphates will be the basis of an important industry for central and Eastern Europe.

Spain.

The use of phosphatic fertilizers in Spain has grown considerably in recent years, but most of the phosphate rock is imported from the United States and Northern Africa.

According to Stone,¹⁷ the only deposits of phosphate developed up to the year 1919 were those in the Province of Caceres which is in the western part of the country midway the Portuguese border. These deposits which have been worked since 1865 are largely a concretionary variety of apatite and occur as veins in limestone, Cambrian schist, and granite. Mining has been done chiefly by open cuts, some of which

¹⁷ Phosphate Rock in 1919, Mineral Resources, part II, p. 219, U. S. Geol. Survey (1921)

are 60 to 70 feet deep. The greatest annual output from these deposits was 200,000 tons, but production gradually fell off and in 1913 amounted to only 3,500 tons. Subsequently the production increased, amounting to 43,000 tons in 1918, but again decreased when mining operations in Northern Africa assumed such huge proportions.

A recent report¹⁸ states that a deposit of phosphate rock has also been discovered in Allama de Murcia, Spain, which is interesting from a geologic and possibly also from a commercial standpoint. The rock is glauconitic in nature and contains from 20 to 30 per cent of tri-calcium phosphate and 7 per cent of potash. The deposit is estimated to contain in the neighborhood of 10,000,000 tons of phosphate.

Japan.

PHOSPHATES OF ASIA.

Phosphate deposits of more or less importance have been worked in certain islands off the coast of Japan, but the annual output was insufficient to meet the agricultural demands of that country.¹⁹

For many years beds of low grade phosphate have been worked in the province of Noto, the Bonin Islands and in Formosa, but the quantity produced has been small. In 1911, after extensive investigations by Japanese interests, phosphate rock was reported on Rasa Island at the extreme end of the Loochoo group.²⁰ This phosphate, which was at first said to be of a grade equal to that on Angaur, Ocean and Nauru Islands, was subsequently found to be so high in iron and aluminum that its use in the manufacture of acid phosphate is both difficult and expensive. The available supply of phosphate on this island is estimated at 2,800,000 tons.

The Japanese, however, control the important deposits of phosphate on Angaur Island as well as those on several of the Marshall Islands formerly operated by German interests. These phosphates are exceptionally high grade and are being actively exploited.

China.

Phosphate deposits, estimated to contain approximately 1,000,000 tons, are reported to occur on the Pratas Islands 170 miles south of

¹⁸ Menéndez, L. Y., Puget (Note on the Formation, Composition and Chemical Properties of the Phosphates of Northern Africa and Spain), *Bol. Inst. Geol. España*, Vol. 43, pp. 331-346 (1923); *Amer. Fert.*, Vol. 62, No. 4, p. 74 (1925).

¹⁹ Statistical Report of Dept. of Agriculture and Commerce, Japan (Annual): Mineral Resources of British Empire, Phosphates, p. 66 (1921), *Min. Inds.* (Annual); The Japanese Acid Phosphate Industry, *Amer. Fert.*, p. 54, April 8 (1922); A New Phosphate Island, *Amer. Fert.*, p. 92, Sept. 10 (1921).

²⁰ *Amer. Fert.*, Oct. 7, 1911.

Hong Kong, China, and in 1913 it was said that a company was planning to exploit these deposits.²¹ No recent reports on these deposits are available.

C. G. Memminger ²² gives a description of some apatite deposits on the Chao Ho River in the province of Kiangsu, Eastern China, ten miles from the seaport of Hsin Pu Cheng. This rock is of a very exceptional grade, containing 90 per cent tricalcium phosphate, and is said to be quite friable and readily ground. No mining is being conducted in this region at present, but it is pointed out that the cheap labor existing in these regions and the exceptional richness of the mineral make it very probable that these deposits will be developed and serve as a source of phosphoric acid for the Japanese market.

²¹ Min. Industry, p. 592 (1914).

²² Chinese Phosphate Deposits, Amer. Fert., Vol. 61, No. 10, p. 27, Nov. 15, 1924.

Chapter 4.

So-called Available Phosphates.

Under the heading of available phosphates are included a number of primary and secondary products resulting from the mechanical and chemical treatment of the natural phosphates just described. The term available, however, is a relative one and is applied to those phosphate carriers the application of which experience has taught us often result in additional crop yields, although the phosphoric acid which they contain is very sparingly soluble in water. While attempts have been made to measure the availability of such phosphates by their solubility in certain weak acids and dilute solutions,¹ no satisfactory laboratory methods have yet been devised which will accurately determine the rate at which these phosphates dissolve in the soil solution or give a true index of their effectiveness under soil conditions.² The laboratory tests for the availability of phosphates therefore are largely empirical, having been built up or evolved by ascertaining what media will dissolve those types of phosphates which have been found effective in field practice.

The two methods generally employed in this country in determining the agricultural availability and trade value of various phosphates are the ammonium citrate and the citric acid tests. The American Association of Official Agricultural Chemists recognizes as available all the phosphoric acid in acid phosphate which is dissolved by a definite volume of a neutral solution of ammonium citrate,³ and in the case of basic slag

¹Williams, C. P., *Chem. News*, **24**, p. 306 (1871); Deherain, P. P., *Am. Agron.*, **17**, p. 445 (1891); Grolach, Max, *Landw. Vers. Stat.*, **46**, p. 201 (1896); Schloesing, T., *Compt. Rendu.*, **131**, p. 149 (1900); Peterman, A., *Recherches de Chem. et Physiol.*, **3**, p. 50 (1898); Hoffmeister, Wilhelm, *Landw. Vers. Stat.*, **50**, p. 363 (1898); Emmerling, Dr., *Bied. Centr.*, **29**, p. 75 (1900); Fraps, G. S., *Jour. Amer. Chem. Soc.*, **28**, pp. 823-834 (1906); Stoddart, C. W., *Wis. Agr. Exp. Sta. Research Bull. No. 2*, pp. 50-60 (1909); Moore, C. C., *Jour. Am. Chem. Soc.*, **24**, p. 79 (1902); Dyer, Bernard, *Jour. Chem. Soc. Trans.*, **65**, p. 115 (1894); Hall, A. D., and Plyman, F. J., *Jour. Chem. Soc. Trans.*, **81**, p. 117 (1902); Maercker, M., *Chem. Zcit.*, **63** (1895); *Jour. Assoc. Off. Agr. Chemists*, **1**, No. 4, pp. 4, 15 (1916).

²Hartwell, B. L., R. I. Exp. Sta. 18th Ann. Rep't, p. 285 (1906); Ellett, W. B., and Hill, H. H., *Va. Polytec. Inst., Agr. Expt. Sta. Ann. Rep't for 1909-10*, p. 44 (1911); Burlison, W. L., *Jour. Agr. Research*, **6**, p. 485 (1916).

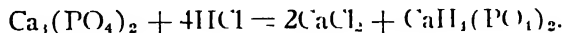
³Official & Tentative Methods of Analyses, A. O. A. C., pp. 1-5 (1919).

has tentatively adopted the Wagner method,⁴ which classes as available the percentage of phosphoric acid dissolved from 5 grams of the sample by 1000 cc. of a 2 per cent solution of citric acid.

Steamed or Degreased Bone.—Steamed or degreased bone is a product obtained by extracting from raw bone the fat which renders the bone so resistant to weathering influences and bacterial action and thus delays its decomposition in the soil and its effectiveness as a phosphate fertilizer. Two general methods are employed in removing the fat from bones. The first consists in treating them with steam under pressure, and the second in using some fat solvent, such as benzine in a closed system wherein the bones are continually bathed in a hot solution of the fat extracting medium. The grease is thus dissolved out and the benzine recovered by distillation and condensation. Not only is the phosphoric acid in fat extracted bone more readily available to crops but the physical condition of the product is such that it can be ground much more easily and effectively, thereby facilitating its uniform distribution in the field. While steamed bone is sometimes treated with sulfuric acid and its phosphate content rendered water soluble and thus more quickly available to crops, the usual practice is to apply it to the field direct. Experience has shown that finely ground steamed bone is undoubtedly an effective phosphate carrier, although usually less than one-half its phosphoric acid is soluble in neutral ammonium citrate solution.

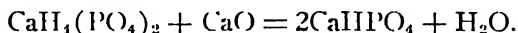
Even if all the degreased bone produced was consumed for fertilizer purposes it would represent only a small proportion of the P_2O_5 entering into agriculture. But by no means all of the degreased bone is used in fertilizers, for bone is a very desirable and much sought raw material in the manufacture of phosphoric acid and monocalcium phosphate for baking powder purposes. A considerable tonnage of bones and certain other by-products of the packing industry is also used in the manufacture of glue and gelatin, which in turn yields a by-product of dicalcium or precipitated phosphate having a high agricultural value.

Dicalcium Phosphate.—After bones have been largely degreased either by a preliminary boiling or by extraction with benzine, they consist largely of tricalcium phosphate and an organic material known as ossein. On leaching degreased bone with weak hydrochloric acid (a 2 to 5 per cent solution) the tricalcium phosphate is completely dissolved, yielding a solution of monocalcium phosphate and calcium chloride, thus:



⁴Idem., p. 14 (1919).

To this solution milk of lime is then carefully added in sufficient quantity to produce dicalcium phosphite, thus:



During the addition of the milk of lime filtered samples of the solution are tested from time to time to avoid an excess of base which would cause the formation of tricalcium phosphate.

The precipitate of dicalcium phosphate is then washed (with the minimum amount of water) free of calcium chloride in a filter press dried and sold either as a fertilizer material or used in the manufacture of bone china.

Dicalcium phosphate dissolves completely in a neutral solution of ammonium citrate and hence is classed as agriculturally available.

The undissolved residue resulting from the acid extraction of the degreased bone is soaked, lined, washed, neutralized and boiled to convert it into glue or gelatin, the manufacturing details of which are ably described by R. H. Bogue,⁵ J. Alexander,⁶ and T. Lambert,⁷ and therefore will not be treated here.

Available Phosphates Produced by Processes Used in Connection with the Iron and Steel Industries.—A number of processes have been patented for producing available phosphates by heat treatment. The various steps being preferably conducted in connection with the production of iron and steel in order to utilize to the best possible advantage a portion of the enormous amount of heat which goes to waste at such plants. These processes are listed in the Appendix, under Table LXIX.

A brief discussion of one or two of those which have features of commercial importance appears desirable.

The processes of Howe and Stead⁸ and of Reese⁹ have for their object the enrichment of slags by the addition of phosphate rock. In both of these processes the phosphate rock is mixed with the slag in the furnace, lime being added if necessary. While there is little doubt that such a procedure would result in a highly phosphatic slag in which the phosphoric acid is available according to certain conventional laboratory tests, and probably also under field conditions, the prejudice against the addition of phosphatic materials to a furnace the prime purpose of which is to produce metal free from phosphorus would be such as to make it impractical to use this method of enriching slags low in phos-

⁵ The Chemistry and Technology of Gelatin, and Glue, 644 pages, McGraw-Hill Book Co. (1923).

⁶ Glue and Gelatin, 236 pages, Chemical Catalog Co. (1923).

⁷ Bone Products and Manures, 284 pages, Scott, Greenwood and Son (1925).

⁸ U. S. Patent 535,204.

⁹ U. S. Patent 714,331.

phoric acid. It has also been proposed to add phosphate rock to the molten slag as it issues from the furnace,¹⁰ the assumption being that there would be a reaction between the rock and the molten slag and the phosphoric acid in the final product would be in an available condition. Up to the present, however, this has not been accomplished successfully and it seems to be largely a question of the mechanical difficulty in obtaining a sufficiently intimate mixture between the two materials to bring about the desired reactions before the slag cools and hardens. The other processes of Reese¹¹ are little more than modified forms of the Thomas and Gilchrist method of manufacturing basic slag for fertilizer purposes, except that phosphate rock is added to the furnace charge to insure the production of a highly phosphatic slag.

Basic Slag.—By far the greatest source of so-called available P_2O_5 for fertilizer purposes, but a product which is used much more extensively in Europe than in this country, is the basic slag obtained as a by-product in the manufacture of steel by either the basic Bessemer or the basic open hearth process. The consumption of basic slag as a phosphate fertilizer is second only to that of acid phosphate and during the late war certain countries, particularly Germany, had to depend largely on this material to meet its agricultural demand for phosphoric acid.

The latest available statistics showing the production of basic slag in the more important European countries are given below in Table XIX.

Basic slag was first produced in efforts to handle highly phosphatic iron ores which were formerly considered unfit for smelting purposes because of the deleterious effect of phosphorus upon steel which is to be used for structural purposes or submitted to heavy strains. In 1878, however, two Englishmen, Thomas and Gilchrist, worked out a process for completely removing this element from pig iron so that high grade steel could be manufactured from these phosphatic ores. Seven or eight years later it was found that the basic slag obtained as a by-product in this process was an excellent phosphatic fertilizer.

The equipment used in the basic Bessemer process consists of a pear-shaped steel vessel (known as a converter) open at the top and provided with a number of inlets in its bottom for the introduction of air under heavy pressure. This vessel may be tilted on a horizontal axis to allow for the introduction of the molten iron and for pouring the slag and steel produced. It is lined with suitable basic materials (dolomite and limestone) which have a strong affinity for phosphoric acid

¹⁰ Jones, W. S., The Importance of Low Grade Basic Slag, Trans. of the Faraday Soc., Vol. 16, Part 2, p. 324 (1921).

¹¹ U. S. Patents 412,792 and 412,793.

TABLE XIX

PRODUCTION (IN METRIC TONS) OF BASIC SLAG IN VARIOUS EUROPEAN COUNTRIES FROM 1913 TO 1921, INCLUSIVE*

Country	1913	1914	1915	1916	1917	1918	1919	1920	1921
Germany	2,250,000	2,067,000	1,540,000	1,800,000	1,750,000	1,500,000	700,000	733,000	953,000
Austria Hungary	50,800	30,900	60,420	85,428
Belgium	655,000	578,000	0	0	0	380,000	380,000	325,000
Great Britain	730,000	480,000	495,000	508,000	575,000	556,230	510,135	585,434	210,000
Russia	40,000	60,000
Sweden ..	18,354	16,688	18,010	13,258	12,173	13,190	11,725	9,390

* Taken from Documentary Leaflets of International Institute of Agriculture, July, 1922



FIG. 15 Tipping Basic Phosphatic Slag from an Open Hearth Furnace

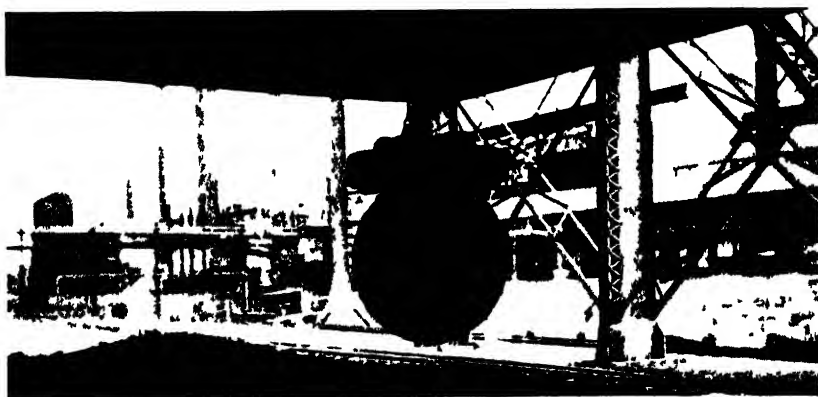


FIG. 16 A Pile of Basic Slag and a 15 Ton Drop Ball Magnet for Breaking up the Material

hearth basic slag containing from 7 to 10 per cent P_2O_5 (20 per cent citric soluble) in the manufacture of which considerable quantities of fluospar (CaF_2) have been employed.

According to von Mayer¹⁴ the composition of basic Bessemer slag falls within the limits given in Table XX.

TABLE XX
COMPOSITION OF BASIC BESSEMER SLAGS ACCORDING TO VON MAYER

Constituent	Percentage Composition
P_2O_5	11.0 to 23.0
SiO_2	3.0 to 13.0
CaO	38.0 to 59.0
Fe_2O_3	6.0 to 25.0
MnO_2	1.0 to 6.0
Al_2O_3	0.2 to 3.7
MgO	2.0 to 8.0
S	0.2 to 11.4

While it is highly essential that the silica content of the slag should be kept down during the "blow" in order to insure the complete elimination of the phosphorus from the steel it has been repeatedly demonstrated that in slags of equal P_2O_5 content those having the higher percentage of silica usually show a greater availability both by laboratory and field tests.¹⁵ It is therefore customary to add silica to the molten slag when it is poured from the converter and Wagner¹⁶ states that the availability of the P_2O_5 is thus increased from 10 to 30 per cent.

The effective fertilizer ingredient in basic slag is generally believed to be tetracalcium phosphate ($Ca_4P_2O_{10}$) and in fact the presence of this compound has been determined by a number of investigators.¹⁶ The mineral "Isoklas" ($Ca_4P_2O_{10} \cdot Ca(OH)_2 \cdot 4H_2O$) which is found with hornstone or brown spar is the nearest approach to tetracalcium phosphate occurring in nature.¹⁷

By no means all of the phosphoric acid present in basic slag is combined as tetracalcium phosphate for other crystalline compounds containing P_2O_5 combined with lime and silica have been identified.^{17a}

¹⁴ *Agricultur Chemie*, Vol. 2, p. 133.

¹⁵ Wagner, *Düngungsfragen*, Vol. 1, p. 28 (1896); Maereker, *Deutsche Landw. Presse*, No. 82, p. 83 (1895).

¹⁶ *Loc. cit.*

¹⁶ Hilgenstock, G., *Stahl u Eisen* (1883); Otto, *Chem. Zeit.*, Vol. 11, p. 255 (1887); Wiley and Krug, *Jour. Anal. Chem.*, Vol. 5, p. 685 (1891), Pritsch, *Mfr. of Chem. Manures*, pp. 202-4 (1911).

¹⁷ Dana, *A System of Mineralogy*, p. 835 (1914).

^{17a} Carnot, Richard and Daubre, *Compt. Rend.*, Vol. 97, p. 136 (1883); Stead and Redsdale, *Trans. Chem. Soc.*, Vol. 51, p. 601 (1887); Kroll, *Jour. Iron & Steel Inst.*, Vol. 2, p. 126 (1911).

Hilgenstock and Carnot¹⁸ found that different types of crystals followed one another in regular sequence in the molten mass and that towards the end of the "blow" when the bath was richer in silica, blue crystals having the composition $P_2O_5.SiO_2.5CaO$ were found. Koll¹⁹ gives the following list of compounds the presence of which has been determined in basic slag.

Silico-carnotite.....	$3CaO.P_2O_5 : 2CaO.SiO_2$
Hilgenstockite.....	$4CaO.P_2O_5$
Steadite.....	$3(3CaO.P_2O_5) : 2CaO : 2CaO.SiO_2$
Thomasite.....	$6CaO.P_2O_5 : 2FeO.SiO_2$

The first of these silico phosphates was later prepared synthetically by Bainbridge²⁰ and found to be very much more soluble in 2 per cent citric acid than tetracalcium phosphate.

Wagner believed that the P_2O_5 in basic slag is in the form of a double salt of calcium phosphate and calcium silicate and that probably some of the P_2O_5 is united with iron as basic iron phosphate. Cameron & Bell²¹ state that the efficiency of basic slag seems to depend chiefly on the degree of fineness to which it is ground and that the tetracalcium phosphate it contains is probably unstable in aqueous solutions. According to Russell²² it is generally believed in Great Britain that the P_2O_5 in basic slag is combined as a silico phosphate which is assumed to have a different physiological action in the soil than the ordinary mineral phosphates.

Whatever the compounds of phosphorus may be in basic slag (free from fluorine), carefully controlled pot and field experiments have shown that the P_2O_5 contained therein is readily available under soil conditions.

When basic slag was first placed upon the market it was customary to sell it on the basis of its total P_2O_5 content and the degree of fineness to which it was ground. These specifications, however, led to the adulteration of basic slag with finely ground phosphate rock which necessitated devising some method by which a mixture of the two materials might be identified. For this purpose Wagner²³ proposed a mixture of dilute ammonium citrate and free citric acid. Later the Union of German Experiment Stations at Kiel in September, 1896, adopted the 2 per cent citric acid test and did away with the total P_2O_5 standard and fineness of product. This test which has also been tenta-

¹⁸ Fritsch, *Min. of Chem. Manures*, p. 205 (1911).

¹⁹ *Jour. Iron & Steel Institute*, Vol. 2, p. 126 (1911).

²⁰ *Carnegie Scholarship Memoirs*, part III, p. 14, Iron & Steel Institute (1920).

²¹ *Bull.* 41, Bureau of Soils, U. S. Dept. of Agric. (1907).

²² *Trans. Faraday Soc.*, Vol. 16, pt. 2, p. 265 (1920).

²³ *Chem. Zeitung*, Vol. 19, No. 63, p. 1419 (1895).

tively adopted in the United States²⁴ was applied after checking the solubility of P_2O_5 in this medium with the results obtained by pot experiments. In the following table given by Lindsey²⁵ it will be seen that in the majority of cases results obtained by these two methods checked fairly closely.

Basic slag is also soluble in carbonated waters and in the following table the results obtained by Reis and Arens and quoted by Fritsch²⁶ show the relative solubility of several slags and various other phosphate-bearing materials in water saturated with CO_2 . It will be noted that in most instances the P_2O_5 in the slags has a much higher solubility than that in bone, phosphorite or even dicalcium phosphate.

TABLE XXI

RELATION BETWEEN THE SOLUBILITY OF THE P_2O_5 OF BASIC SLAG IN 2 PER CENT CITRIC ACID AND ITS AVAILABILITY AS SHOWN BY POT EXPERIMENTS

Brand of Slag Number	Availability of P_2O_5	
	In 2 Per Cent Citric Acid	In Pot Tests
1	100	100
2	85	80
3	81	72
4	72	72
5	73	66
6	76	63
7	39	40
8	48	38
9	42	38
10	45	31
11	38	30

According to Kaysser²⁷ the availability of basic slag is materially affected by the rate at which the material is cooled after being tapped from the furnace. The P_2O_5 in slags which have been rapidly cooled shows a higher solubility in 2 per cent citric acid than that in slags which are allowed to cool slowly. This greater solubility of the former slags is due it is claimed to the formation of less basic phosphates than occur in the slowly cooled slag mass. Fritsch²⁸ on the other hand states that basic slag which is allowed to cool slowly in large blocks is as a rule much more readily ground than that which has been rapidly cooled by pouring it into relatively thin layers.

²⁴ Loc. cit.

²⁵ Mass. Exper. Sta., 22nd Annual Report, part 1, p. 79.

²⁶ Mfr. of Chem. Manures, p. 209 (1911).

²⁷ Chem. Ztg., Vol. 44, p. 826 (1920).

²⁸ Mfr. of Chem. Manures, p. 212 (1921).

TABLE XXII
SOLUBILITY OF BASIC SLAG IN WATER SATURATED WITH CARBONIC ACID

	Content of			Quantities Dissolved by 10 Liters of Water Saturated by CO ₂			Comparative Solubility		
	SiO ₂	P ₂ O ₅	CaO	SiO ₂	P ₂ O ₅	CaO	SiO ₂	P ₂ O ₅	CaO
	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
Basic slag I	2.57	18.30	48.08	1.51	4.19	19.37	58.8	22.9	39.8
" " II	5.20	15.07	48.82	3.15	5.66	24.84	50.9	37.4	51.0
" " III	2.85	21.30	48.36	2.11	7.55	27.85	74.0	35.5	57.5
" " IV	4.05	18.33	50.35	2.27	6.81	24.19	56.0	37.5	48.0
" " V	7.67	16.32	47.98	4.22	7.89	24.54	56.3	48.1	51.1
" " VI	6.93	15.74	48.15	3.55	4.50	25.08	51.2	28.7	52.0
" " VII	5.54	24.00	46.35	3.05	7.59	19.36	86.1	31.6	41.7
Shell slag	18.15	13.47	44.10	4.99	3.45	15.17	27.4	25.5	34.4
Prepared slag	6.58	24.95	51.25	4.07	7.79	21.00	61.8	31.2	40.9
Scheibler's precipitate	8.02	33.36	31.10	0.62	7.36	9.37	7.7	22.0	30.1
Hoyermann's precipitate	5.70	14.93	34.05	1.29	4.96	19.96	22.7	33.0	58.5
Dicalcic phosphate of lime	51.09	41.03	8.57	6.95	16.8	16.8
Tricalcic phosphate of lime	43.26	51.45	5.41	7.04	12.5	13.6
Tetralcic phosphate of lime	36.85	62.70	15.52	33.27	42.1	53.0
Degreased cattle bones	25.23	32.75	7.19	9.65	28.5	28.9
Bone ash made from above bones	41.71	55.75	2.29	3.29	5.5	5.9
Phosphorite	1.77	32.00	45.36	0.10	1.00	1.67	5.7	3.1	3.8

Like all materials, however, which are not readily soluble in water the distribution of basic slag in the soil and its effectiveness as a fertilizer are necessarily dependent upon the degree of fineness to which it is ground. On account of its hardness and also because of the metal contained therein machinery of the type usually employed for grinding phosphate rock is not adapted for pulverizing slag. Ball or tube mills therefore are used and a product 90 per cent of which will pass a 100 mesh screen thus obtained.

Considerable concern is being expressed by English agriculturists²⁹ because of the tendency to replace the basic Bessemer method by the basic open hearth process which is said to be more economical. The chief aim of the steel manufacturer is to produce metal at the lowest possible cost and the added value of the basic slag produced by the former process is insufficient to offset the saving effected in manufacturing the main product by the latter method.

Russell³⁰ states that from the steel manufacturer's viewpoint basic Bessemer slag is relatively unimportant. Only about 400 lbs. of this slag are obtained for every ton of steel produced and where this amount of steel brings at least \$50.00, the 400 lbs. of slag are worth only about \$1.12 to the steel manufacturer and less than \$4.00 even after being graded, ground and sacked.

Not only is the P_2O_5 content of the average basic open hearth slag considerably lower than that of basic Bessemer slag but in recent years the manufacturer has been adding fluorspar (CaF_2) to the metal bath which decreases greatly the citric solubility and agricultural availability of the slag due to the formation of compounds analogous to apatite.³¹

In order to meet these changing conditions in the manufacture of steel without sacrificing the agricultural availability of basic slag, and also with a view to increasing the percentage of available P_2O_5 in slags produced from iron ores low in phosphorus, a number of schemes have been suggested for the enrichment of this important by-product of the steel industry.

One of these general schemes is to add a certain amount of phosphate rock to the charge of either the basic Bessemer converter or the basic open hearth furnace. In the process of Howe and Stead³² it is proposed to charge preheated phosphate rock into the basic Bessemer converter along with sufficient lime to insure a slag as basic as tetra-calcium phosphate. The molten iron is then poured on this mass and the

²⁹ Trans. of Faraday Society, Vol. 16, pt. 2, p. 263 (1920).

³⁰ Robertson, G. S., *Basic Slags and Rock Phosphates*, Cambridge Agric. Monographs, preface p. viii, by E. J. Russell (1922).

³¹ Stead, Bainbridge and Jackson, Trans. of Faraday Society, Vol. 16, pt. 2, p. 302 (1920); Bainbridge, Carnegie Scholarship Memoirs, pt. 3, p. 14 (1917).

³² U. S. Patent 535,204 (1895).

"blow" conducted in the usual way. The inventors claim that in this process a slag very rich in citric soluble P_2O_5 is obtained. While there is little doubt that such a procedure would result in a highly phosphatic slag in which the phosphoric acid is readily available under field conditions, the prejudice against the addition of phosphatic materials to either the open hearth or Bessemer furnace the prime purpose of which is to produce metal free from phosphorus renders it impractical to use this method of enriching slags low in phosphoric acid. Moreover, Jones³³ states that the solubility of the added phosphate is not increased in the open hearth furnace unless the charge is allowed to remain on the hearth too long for economical operation.

With the same end in view it has been proposed to add finely ground phosphate rock to the molten slag as the latter is tapped from the furnace³⁴ the assumption being that there would be a reaction between the rock and the molten slag and the phosphoric acid in the final product would be in an available condition. Up to the present, however, this has not been accomplished successfully and it seems to be largely a question of the mechanical difficulty in obtaining a sufficiently intimate mixture between the two materials to bring about the desired reactions before the slag cools and hardens. The senior author, however, in a series of experiments³⁵ on the enrichment of slags obtained both citric soluble phosphoric acid and potash by smelting suitable mixtures of basic open hearth slag, phosphate rock and feldspar and it would seem that this method of utilizing the heat energy of molten slags should be eventually worked out.

Reese³⁶ suggests mixing phosphate rock with basic open hearth slag and 5 per cent of manganese dioxide and the fusion of this mixture in a cupola furnace under oxidizing conditions, but since this process apparently involves first cooling the slag so it may be broken up and mixed with the phosphate it hardly appears to the authors as economical.

Another suggestion which has been made is to add phosphate rock or low grade phosphatic slag to the charge in the blast furnace in order to produce a pig iron rich in phosphorus which may be subsequently dephosphatized in the steel furnace with the production of a highly phosphatic slag. A modification of this process has been patented by W. R. Walker³⁷ but it is doubtful if this method could be successfully used except in connection with the basic Bessemer process.

It seems to be generally believed, however, that the most practical

³³ Trans. of Faraday Society, Vol. 16, pt. 2, p. 325 (1920).

³⁴ Jones, W. S., The Importance of Low Grade Basic Slag, Trans. of the Faraday Soc., Vol. 16, Part 2, p. 324 (1920).

³⁵ Bull. 95, Bureau of Soils, U. S. Dept. Agriculture (1913).

³⁶ U. S. Patent Nos. 714,330, 714,331 (1902).

³⁷ U. S. Patent No. 1,299,072 (1919).

means of obtaining a highly phosphatic slag when manufacturing steel by the basic open hearth method is to use a duplex process. In the Bertrand-Thiel process ³⁶ two furnaces are used, in the first of which pig iron without scrap is smelted with highly basic materials. Practically all of the phosphorus and silicon are removed from the metal in this primary furnace and a highly phosphatic slag is obtained. The metal is then transferred to a secondary furnace containing limestone scrap and fluorspar and the refining of the steel thus completed. The American Duplex method as described by McCaffrey ³⁹ which is successfully practiced in this country is almost the reverse of the above since the metal is first desiliconized in an acid Bessemer converter, the siliceous slag tapped off and the metal then charged to a basic open hearth furnace in order to remove the phosphorus. It is understood that the one concern ⁴⁰ which manufactures basic phosphatic slag in the United States employs a duplex process.

A number of other processes have been patented for producing available phosphates by heat treatment, the various steps being preferably conducted in connection with the production of iron and steel in order to utilize to the best possible advantage a portion of the enormous amount of heat which goes to waste at such plants. These processes are listed in the Appendix, under Table LXXVI.

The use of basic slag in American agriculture is rather limited, and most of that which is consumed is imported from abroad. This is not due to lack of appreciation of the merits of this product but to the fact that the bulk of the iron ores used for the manufacture of steel are so low in phosphorus that the slags obtained contain only very small percentages of phosphoric acid. In addition to this, our enormous deposits of phosphate rock, and large output of sulfuric acid have made it possible to obtain soluble phosphates at such a low price that it is difficult for basic slag to compete with them.

Calcination Processes for the Production of Available Phosphates.

With the idea of doing away with the use of sulfuric acid for the manufacture of soluble phosphates, investigators have spent considerable time and effort on calcination processes wherein phosphate rock is heated with one or more cheap reagents intended to either bring about the decomposition of the mineral or so alter its physical structure that the product conforms to the conventional tests specified as measures of agricultural availability. While available phosphates produced by calcination processes would meet a demand in certain sections where a

³⁶ Transactions of the Faraday Society, Vol. 16, pt. 2, p. 326 (1920).

³⁹ Blast Furnace and Steel Plant, Vol. 7, p. 287 (1918).

⁴⁰ Tennessee Coal and Iron Railroad Co., Birmingham, Ala.

popular prejudice exists against fertilizers of an acid nature, these processes have been investigated chiefly for economic reasons, since they seem to offer a means of utilizing low grade phosphate rock or mineral phosphates containing certain impurities, rendering them unfit for treatment with sulfuric acid. Even where lower grades of phosphate are treated by these calcination processes, the final products usually contain higher percentages of phosphoric acid than ordinary acid phosphate, and therefore if the cost of producing the unit of available phosphoric acid were no less than that obtained by the sulfuric acid method, the saving effected in transportation and handling charges on the more concentrated products should give the latter a considerable economic advantage.

While much research work has been conducted on calcination processes, there is comparatively little recorded outside of the patent literature. Some of the processes described below have been unquestionably tried out on a commercial or semi-commercial scale, and in some instances successful results have been reported, but apparently certain mechanical or chemical problems have arisen which make it difficult to obtain a product in which the phosphoric acid is uniformly available.

Phosphate Rock, Silica and Lime.—There are five patents in which it is claimed that the heating of phosphate rock with silica alone or with silica and an alkaline earth compound brings about reactions in which the phosphate is rendered citrate soluble. In the process of DeChalmot⁴¹ and Downs⁴² mixtures of phosphate rock and sand are heated with the idea of bringing about a combination between the silica and phosphate rock, producing a compound somewhat analogous to that found in the basic slag obtained by the basic open hearth or basic Bessemer process. Temperatures, however, are not raised sufficiently high to form even a clinker, and it hardly seems possible that any substantial conversion of the calcium phosphate into more complex compounds could be brought about under the conditions mentioned. No particular time for the heating process is specified, but the final product is said to contain an average of 20 to 22 per cent of P_2O_5 , all of which is soluble in 2 per cent citric acid.

In the process of Stead⁴³ both lime and silica are mixed with phosphate rock and the mass heated to a smelting temperature. In order to reduce the melting point of these mixtures, mill cinder or some iron-bearing mineral is added. The inventor claims that a product containing a compound of the definite formula $Ca_5P_2SiO_{12}$ is obtained, which is

⁴¹ U. S. Patent No. 588,266 (1897).

⁴² U. S. Patent No. 1,120,917 (1914).

⁴³ U. S. Patent No. 589,197 (1897).

readily available under soil conditions. In Zilk's process,⁴⁴ finely ground coke and limestone are mixed with phosphate rock, the mass moistened with water to form a paste and heated in a rotary kiln to 1300° to 1400° F. for a period not exceeding 1½ hours. It is claimed that the resultant mass which may be easily crushed contains P_2O_5 in a readily available form. The inventor states that care must be taken to prevent overheating of the mass and the production of hard clinkers.

The experience of the senior author has been, however, that in heating mixtures of phosphate rock and siliceous materials without the addition of an alkali metal salt, it is difficult to obtain a product in which the phosphoric acid is available until a sufficiently high temperature (1400° to 1500° C.) is attained to smelt the mass. Moreover, unless the charge is quite basic, a partial volatilization or loss of phosphoric acid may take place at high temperatures, particularly if a reducing agent such as coke is present.

Phosphate Rock and Potash Silicates.—With the idea of obtaining both potash and phosphoric acid in available forms, a number of investigators have proposed mixing a potash bearing mineral such as feldspar with the phosphate charge and heating these mixtures to a temperature where double decomposition occurs. Typical examples of such processes are those of Meriwether,⁴⁵ Cowles,⁴⁶ and Delacourt,⁴⁷ in none of which is a soluble alkali metal compound employed. Cowles⁴⁸ proposes to heat in a rotary kiln a mixture of phosphate rock and a potash bearing silicate to a temperature ranging between 1000° and 1700° C. The two minerals are mixed in such proportions that there are present two molecular weights of lime for each molecular weight of silica. The inventor assumes that the phosphoric acid in the resultant product is combined with potash and alumina and that the lime is largely in the form of silicate. He further claims that while both the potash and phosphoric acid may be readily leached from this calcined mass by means of a mineral acid, the material may be used as a fertilizer by grinding it and applying it directly to the soil without further treatment.

Delacourt's process is very similar to that just described, except that free silica is mixed with the charge in addition to that present in the potash silicate. This investigator further stipulates a temperature of 1000° to 1100° C. and the maintenance of oxidizing conditions to prevent the reduction of phosphoric acid. The product, it is claimed, consists of a mixture of potassium calcium phosphate and calcium silicate.

In some rather exhaustive experimental work conducted by the

⁴⁴ U. S. Patent No. 1,236,812, 1,247,059 (1917). .

⁴⁵ U. S. Patent No. 1,016,352 (1912).

⁴⁶ U. S. Patent No. 1,126,408 (1914).

⁴⁷ U. S. Patent No. 1,282,385 (1918).

⁴⁸ Loc. cit.

TABLE XXIII
COMPOSITION OF FELDSPAR AND PHOSPHATIC LIMESTONE USED

Material	SiO ₂		AlO ₃		CaO		K ₂ O		Na ₂ O		P ₂ O ₅		CO ₂	
	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
Feldspar	65.7	18.4	37.1	13.7	2.2
Phosphatic limestone	32.4	20.0	10.5

TABLE XXIV
PROPORTIONS IN WHICH INGREDIENTS WERE MIXED AND ANALYSES OF MELTS OBTAINED

Sample No.	Amount of Material Used				Tem- perature ° C.	Time of Heating Hours	Properties of Fusion	Analysis of Melts			
	Feldspar	Phos- phatic Lime- stone	Fe ₂ O ₃	MnO ₂				P ₂ O ₅ Soluble in Citric Acid	Total P ₂ O ₅	K ₂ O Soluble in Citric Acid	Total K ₂ O
	Per Cent	Per Cent	Per Cent	Per Cent				Per Cent	Per Cent	Per Cent	Per Cent
333 S A.....	46.8	37.5	9.4	6.3	1,200	1½	Viscous	1.82	8.50	5.98	6.76
333 S B.....	46.8	37.5	9.4	6.3	1,400	7½	Liquid	7.22	7.21	6.50	6.48
333 S C.....	46.8	37.5	9.4	6.3	1,400	1½	Less liquid	2.50	3.76	Lost	5.48
333 S D.....	46.8	37.5	9.4	6.3	1,400	4½	Viscous	1.20	2.88

senior author,⁴⁹ it was found that by heating the proper proportions of feldspar and phosphatic limestone with the addition of small amounts of iron and alumina to lower the melting point of the mixture, slags could be obtained in which the bulk of both the potash and phosphoric acid present was in a condition soluble in 2 per cent citric acid.

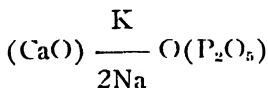
While citric soluble potash was readily obtained by heating various mixtures of feldspar and phosphatic limestone over a wide range of temperatures, the limits within which the maximum yields of citric soluble phosphoric acid are obtained are quite narrow, both in respect to the proportion of the ingredients in the mixture and the length of time of heating.

In Table XXIII is given the composition of the materials used in these experiments, and in Table XXIV the proportions employed for the best results, and the effect of various temperatures on the availability of the phosphoric acid and potash.

It is shown in Table XXIV that when the mixture was heated to 1200° C. for about twenty minutes the fusion was not complete and only a little more than 21 per cent of the total phosphoric acid present was citric soluble; over 88 per cent of the potash, however, was soluble in the same medium. Upon raising the temperature to 1400° C. and maintaining it there for twenty minutes the fusion became quite fluid, and, although small amounts of potash and phosphoric acid were lost through volatilization, the remainder of these ingredients was entirely soluble in 2 per cent citric acid. After heating the mixture for one hour longer at the same temperature almost 50 per cent of the phosphoric acid and more than 15 per cent of the potash were volatilized, and upon heating for three hours more the phosphoric acid was still further reduced.

The sample richest in citric soluble phosphoric acid and potash (33S B) was submitted to a microscopic examination and found to be isotropic and possessed all the external characteristics of a glass.

According to a recent report⁵⁰ a product known as Rhenania Phosphate is being manufactured in commercial quantities in Germany by a process similar to those just described. Briefly, this method consists in heating to 1200° to 1300° C. an intimate mixture of phosphate rock, limestone and a potash silicate such as phonolite. The main product is said to have the approximate formula



⁴⁹ Waggaman, W. H., Bull. 143, U. S. Dept. Agric. (1914).

⁵⁰ Rhenania Phosphate, Zeitschrift für Angewandte Chemie, October 3, 1922; abstracted and translated by S. J. Lloyd in the American Fertilizer, Vol. 57, No. 13, p. 38, December 30 (1922).

but there are also present in the resultant mass, calcium silicate and aluminate.

The material is discharged from the furnace or kiln as a brown sinter or clinker and after cooling is finely ground and sold as a potash-phosphate fertilizer.

The composition of this product varies according to the nature and purity of the minerals employed but is said to lie between the following limits.

$$\begin{aligned} \text{P}_2\text{O}_5 &= 15 \text{ to } 25 \text{ Per cent} \\ \text{K}_2\text{O}, \text{Na}_2\text{O} &= 8 \text{ to } 15 \text{ Per cent} \\ \text{SiO}_2 &= 10 \text{ to } 20 \text{ Per cent} \\ \text{CaO} &= 35 \text{ to } 40 \text{ Per cent} \end{aligned}$$

While the percentage of water soluble phosphoric acid in Rhenania Phosphate is very low, it is claimed that 90 per cent is available according to the 2 per cent citric acid test, the bulk of it is soluble in alkaline ammonium citrate (which has little effect on basic slag), and 75 per cent is dissolved by carbonated waters. It is also said that the potash in this product is in an available form but no mention is made of the test applied in determining the availability of this latter fertilizer constituent.

Phosphate Rock and an Alkali Metal Hydroxide or Carbonate. Wiborgh,⁵¹ Conner,⁵² Newberry,⁵³ Galt,⁵⁴ and Stoppani and Volpato⁵⁵ have proposed heating to bright redness in a suitable furnace intimate mixtures of finely ground phosphate rock and an alkali metal hydroxide or carbonate until a sintered or semi-fused mass is obtained.

While the same general principle is employed in all of the processes listed above the mode of procedure and the proportions of the several ingredients used are varied by the inventors. There also appears to be a wide difference of opinion regarding the chemical reactions involved.

Wiborgh's process was apparently designed to treat Norwegian apatite and consists in mixing 100 parts of this mineral with 32 parts of sodium carbonate (or its equivalent of NaOH) and raising the mass to a red or yellow heat in order to obtain what he terms tetra-calcium-sodium phosphate to which he assigns the following formula:



This product is said to be insoluble in water but readily soluble in ammonium citrate.

⁵¹ U. S. Patent No. 601,089 (1898).

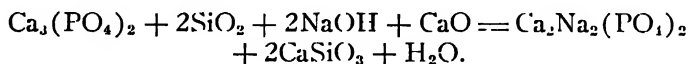
⁵² U. S. Patent No. 931,846 (1909); 1,042,400; 1,042,401 (1912).

⁵³ U. S. Patent No. 978,193 (1910).

⁵⁴ U. S. Patent No. 1,016,989 (1912).

⁵⁵ U. S. Patent No. 1,267,473 (1918).

In Connor's process one part of soda ash and two parts of lime are mixed with five parts of finely ground siliceous phosphate rock, the mass made into a paste with water, and heated for 1½ hours at a temperature ranging between 1500° and 2000° F. The reaction which is said to take place is expressed as follows:



Galt proposes to utilize the lime-mud which is a waste product obtained in the manufacture of caustic soda and contains a sufficient quantity of the latter compound to make it useful as a reagent in treating phosphate minerals. He suggests, however, that if the quantity of NaOH present in the lime-mud is insufficient, that it be reenforced with soda ash. He claims that by heating the various ingredients in the following proportions to a temperature of 2000° F. that the phosphate rock is decomposed and either sodium pyrophosphate or trisodium phosphate is formed:

Low grade phosphate rock	1256 pounds
Lime-mud	1570 "
Soda ash	410 "
Water	314 "

In the patent of Stoppani and Volpato, the process under which the Italian fertilizer known as "Tetraphosphate" is manufactured,⁵⁰ the inventors claim that by quenching the calcined product with water as it is discharged from the kiln the availability of the phosphoric acid contained therein is appreciably increased.

Since the base used in these processes is not combined with a strong acid, there is little doubt that reactions would take place which would actually change the composition of the phosphate rock, the product being more basic than the original mineral and probably having both sodium and calcium combined with phosphoric acid. On the other hand, it would seem that the use of the relatively large quantities of high priced soda compounds (Na_2CO_3 and NaOH) specified in several of these patents and the prolonged heating of the mixtures would tend to offset largely any saving effected from the use of lower grades of phosphate rock. At least one of these processes was tried out in a commercial way, in Tennessee some years ago but apparently was not successful.

⁵⁰ Tetraphosphate, a special Italian fertilizer; American Fertilizer, Vol 51, p. 58, Nov. 22, 1919; Bruno, A., Compt. Rend. Acad. Agr., Vol. 4, pp. 322-4 (1918).

Phosphate Rock and an Alkali Metal Salt. Probably the calcination processes which have received the most thorough investigation are those in which an alkali metal compound (usually Na_2SO_4 or NaHSO_4) is mixed with phosphate rock in relatively small quantities and heated in a furnace to a temperature where the acid radical of the salt is volatilized and frequently part of the alkali base as well. This general scheme is varied by a number of inventors, silica, silicates or carbonates being used in addition to the alkali salt mentioned above. Typical examples of these processes are furnished by the patents of Newberry and Barrett,⁵⁷ Newberry and Fishburne,⁵⁸ Landis,⁵⁹ Soper,⁶⁰ Kreiss⁶¹ and Meyers.⁶² Practically all of these inventors agree that in order to obtain a product in which P_2O_5 is readily available it is necessary that the mass be thoroughly impregnated with the alkali metal compound during the early stages of the heating, and that the mixture be maintained in a porous condition throughout the operation. The temperatures specified by the various inventors range all the way from 1000° to 1500° C.

Of these processes the one which has recently attracted considerable attention is that of A. L. Kreiss. In his first patent, the inventor claims the method of producing available (citrate soluble) phosphoric acid and water soluble potash, consisting in intimately mixing finely ground phosphate rock (1 to 2 parts) and feldspar ($\frac{1}{2}$ to 1 part) with one or more soluble alkali salts ($\frac{1}{2}$ to 1 part) and heating the mixture in a rotary kiln with a reducing flame. In his second patent, an improvement over the first method is claimed since the expense of shipping and grinding the phosphate is obviated and a more intimate mixture of the rock materials obtained by impregnating the unground phosphate with the solution of alkali metal salts in the cooler part of the rotary kiln where the temperature ranges between 100° and 500° C. It is said that the impregnated phosphate nodules or lumps burst open or disintegrate as these enter the hotter zone of the kiln (where the temperature ranges between 500° and 1070° C.) and the mass finally reacts and forms citrate soluble phosphoric acid and water soluble potash. At least one plant has been erected in Florida for producing this material on a commercial scale and some of the product is now offered on the market.

Fishburne⁶³ in a relatively recent article on calcined phosphates re-

⁵⁷ U. S. Patents Nos. 1,158,711; 1,162,802; 1,162,944 (1915); 1,173,303; 1,174,176 (1916).

⁵⁸ U. S. Patent No. 1,194,219 (1916).

⁵⁹ U. S. Patent No. 1,094,857 (1914).

⁶⁰ U. S. Patent No. 1,281,681 (1918); 1,396,149; 1,396,975 (1921).

⁶¹ U. S. Patent No. 1,366,569 (1921); 1,413,168 (1922).

⁶² U. S. Patent No. 1,578,339 (1926).

⁶³ Another Process for Calcining Phosphate Rock, American Fertilizer, Vol. 62, p. 21, May 2, 1925.

views the patents owned or controlled by him and describes the conditions under which he considers the best results are obtained.

According to his experience, it is highly important to have the mixture of phosphate rock and alkali metal salt constantly agitated during the heating process and a stream of gas sweeping over and through the mass. He also states that in order to obtain the maximum quantity of available P_2O_5 , the final product should not be fused but discharged in the form of a porous clinker which can be readily crushed between the fingers. He claims that the type of apparatus best suited for carrying out this calcination process is the direct fired rotary kiln.

The following description of the reagents used and the method proposed for producing calcined phosphates is quoted from Fishburne's article:

"As a practical example of our process, we take ordinary phosphate rock and pulverize it; then we add to it from 5 to 15 per cent of its weight of one of the reagents above named, or of a mixture of two or more such reagents. We prefer to use sodium sulphate or bisulphate on account of the cheapness of these reagents, and the ease with which they undergo decomposition under the conditions of calcination herein described. The mixture is then so prepared that it will become porous, and it is then introduced gradually into the upper or feed end of a revolving cylindrical kiln, lined with refractory material preferably of a basic character and internally heated by a flame of coal dust, oil or gas. The kiln is slightly inclined toward the fire end, and revolves at a rate of about one revolution in one or two minutes.

"The fuel is fed into the kiln in intimate mixture with air, and additional air is admitted in such amount that the fuel is completely consumed in the lower part of the kiln, and that a moderately oxidizing atmosphere prevails throughout the interior space, care being taken to avoid admitting any considerable excess of air above that required for perfect combustion. The temperature in the hottest zone, at about one-fourth the length of the kiln from the fire end, is maintained at about 2500° F. (1482° C.), but varies somewhat according to the more or less refractory character of the material treated. Obviously, there can be considerable variation in the temperature and time and quality and quantity of reagent without departing from the spirit of this invention. The temperature should be regulated so as to bring the material to a sintered or semi-fused and porous condition, and to yield a product of maximum and practically complete citrate-solubility.

"In the first stage of the heating the temperature of the charge increases rapidly, and under the combined action of heat, agitation and intimate contact with a rapid current of hot gases the alkali-metal compound is rapidly decomposed, with evolution of its acid or other volatile

constituents. This action takes place actively at a temperature of about 2000° F. (1093° C.), provided the material is porous and the current of hot gases sufficiently rapid. Under these conditions such alkali-metal compounds as hydrate, sulfate or carbonate, which are scarcely affected by heating to much higher temperatures when at rest, are rapidly decomposed with evolution, respectively, of water, sulfur dioxide, oxygen, and carbon dioxide, leaving a residue of alkali-metal oxide, which we term 'residual alkali.'

"The volatile constituents may be said to be 'blown out' of the salts by contact with the current of hot gases. It is probable that the residual alkali enters into combination with the phosphate of lime, forming an alkaline-lime phosphate, which is again in large measure decomposed at the higher temperature of the later stage of the process, and that this combination and subsequent decomposition plays an important part in the conversion of the phosphate into citrate-soluble condition.

"In the final stage of calcination a temperature of about 2500° F. (1482° C.) is required, and in this stage, under the combined action of heat, agitation and intimate contact with a rapid current of highly heated gases, the residual alkali is in turn and in large measure volatilized, and simultaneously with the expulsion of alkali the percentage of citrate-soluble phosphoric acid rapidly increases, until, with proper adjustment of temperature and duration of heating, the conversion to citrate-soluble condition becomes practically complete, only traces of insoluble phosphoric acid remaining.

"The product of the operation conducted as above described appears in the form of brown masses or fragments, extremely porous and light, and so soft that it can be crushed to powder by pressure of the fingers. During the entire course of the calcination the expulsion of the volatile constituents of the alkali-metal compound and of the residual alkali tends to prevent overheating and fusion of the material. This expulsion takes place normally and rapidly if the material is exposed to, and penetrated by, a rapidly moving current of hot gases; for example, such a current as is produced by introducing the fuel at the lower end of the kiln in admixture with a current of air under four or five ounces pressure, and by maintaining a strong draft in the stack at the upper end of the kiln.

"Under these conditions the material remains in a porous and light condition throughout its passage through the kiln, and the volatile constituents of the alkali-metal salt are completely expelled in the zone of moderate heat. The residual alkali is chiefly expelled in the final stage of heating, and the phosphate is rendered practically completely citrate-soluble. The soft, porous clinker then passes out of the kiln, is cooled

and ground to a powder. It is then ready as a fertilizer or for mixture with other ingredients to make complete fertilizers. On the other hand, if the current of hot gases is slow and sluggish or does not freely penetrate the charge, little or no decomposition and expulsion of the alkali-metal salt takes place, the material fuses or sinters together into impervious masses, and comparatively little conversion into citrate-soluble condition is effected."

In the patent recently issued to H. H. Meyers⁶⁴ the inventor claims to obtain the desired porosity and availability of the P_2O_5 in a calcined phosphate by first sintering a finely ground mixture of an alkali metal salt, phosphate rock and coke in a Dwight and Lloyd sintering machine, thereby effecting a partial conversion of the P_2O_5 into a citrate soluble form. The sinter is then crushed and the porous lumps heated in a rotary kiln to $1400^{\circ} C.$ for 20 minutes or to $1250^{\circ} C.$ for 30 minutes.

The proportions of the ingredients employed in producing the sinter are as follows:

Phosphate rock	100 parts
Niter cake	30 "
Powdered coke	9 per cent

After calcining the material is ground to pass a 60 mesh screen and is said to be in a form readily adapted for use either directly or as an ingredient of mixed fertilizers.

Undoubtedly citrate soluble phosphoric acid can be produced by calcination methods but while a number of the processes described under this general heading have seemed to offer considerable promise in laboratory tests, it has been found that when tried out on a commercial scale considerable difficulty is experienced in obtaining products which have a uniform availability in respect to their phosphoric acid content.

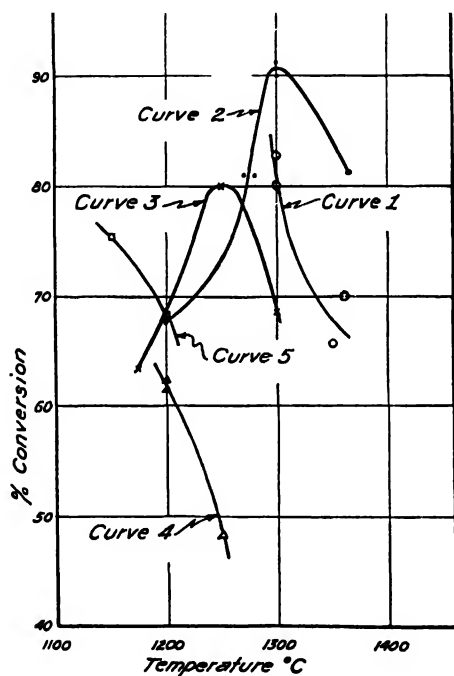
Guernsey and Yee⁶⁵ have conducted a rather complete investigation of the conditions under which phosphate rock is rendered citrate soluble by calcining with small quantities of sodium salts (Na_2SO_4 , $NaHSO_4$, and Na_2CO_3) in the presence and absence of a reducing agent. Their conclusions are that the temperature range within which the maximum conversion of P_2O_5 to a citrate soluble form occurs is rather narrow for each type of salt and for each proportion used.

They state that the optimum temperature for any charge is that at which a sinter (but not a slag) is obtained. In the case of sodium sul-

⁶⁴ Loc. cit.

⁶⁵ The Preparation and Chemical Nature of Calcined Phosphate, Ind. & Eng. Chem., Vol. 16, No. 3, p. 228 (1924).

fate (10 to 20 per cent) this temperature is close to 1300° C. and with sodium carbonate somewhat lower. The results of this investigation should prove of considerable value to those contemplating the manufacture of calcined phosphates for they show pretty conclusively how and why such products when manufactured on a commercial scale vary so greatly in citrate solubility.



	Phosphate Rock	Na ₂ SO ₄	Carbon	Water
Curve 1	100	10	15	0
Curve 2	100	20	15	0
Curve 3	100	30	15	22.5
Curve 4	100	55	27	0
Curve 5	100	224	0	0

FIG. 19.—Conversion of P_2O_5 in Mixtures of Phosphate Rock Carbon and Alkali Metal Salts into Citrate Soluble Form at Various Temperatures.

In the following chart (Figure 19) taken from the article of these writers the conversion of P_2O_5 into a citrate soluble form at various temperatures and with various proportions of the reacting ingredients is graphically illustrated.

A number of hypotheses have been offered in explanation of the conversion of phosphate rock into a citrate soluble form by these cal-

cination processes, one being that a double salt of sodium (or potassium) calcium phosphate is formed. But the small percentage of the alkali metal salt added (15 to 20 per cent) would not be sufficient to convert the whole of the phosphate into a definite double salt. Several of the inventors do not attempt to explain the chemistry of their processes for the reactions involved are not clear. It is claimed that the alkali salt added in some instances is almost entirely driven off at the temperatures attained in the kiln, leaving the phosphate charge practically intact. If this is so the change which takes place under the conditions mentioned may be largely physical and the phosphate which remains is in a condition somewhat analogous to freshly precipitated tricalcium phosphate which is known to exhibit a high degree of availability according to the conventional laboratory tests.

Available Phosphates by Electrolysis.

Up to the present time only five American patents have been issued dealing with the production of available phosphoric acid by electrolytic processes. Of these, four are designed to produce citrate soluble, and the fifth water soluble phosphoric acid. The processes under this heading may be divided into two classes: (1) Those in which the phosphate rock is smelted with a suitable flux and the current passed through the molten charge; and (2) those in which some water soluble salt or acid is used as an electrolyte and the ground phosphate rock suspended or dissolved in the solution and the electrolysis conducted in the wet way. A list of these patents is included in Table LXXIII of the Appendix.

Probably the process under this heading which has attracted the most attention is that of Palmaer and Wiborgh⁶⁶ which may be briefly described as follows:

Perchloric acid and sodium hydroxide are first produced by electrolyzing a solution of sodium perchlorate in a diaphragm cell. Phosphate rock is then added to the anode solution (perchloric acid) and the resultant solution filtered. One half of the cathode solution (sodium hydrate) is then added to this filtrate resulting in the precipitation of dicalcium phosphate and the formation of sodium perchlorate again. Into the other half of the cathode solution a stream of carbon dioxide is led and then this solution (Na_2CO_3) is added to the solution decanted from the dicalcium phosphate precipitate, thus precipitating calcium carbonate and completely regenerating the sodium perchlorate.

The chemical reactions involved in this process may be graphically represented thus:

⁶⁶ U. S. Patent Nos. 707,886 (1902); 748,523 (1903).

- (1) $\text{NaClO}_4 + \text{H}_2\text{O} + \text{Elect Current} = \text{HClO}_4 + \text{NaOH}$
- (2) $6\text{HClO}_4 + \text{Ca}_3(\text{PO}_4)_2 = 2\text{H}_3\text{PO}_4 + 3\text{Ca}(\text{ClO}_4)_2$
- (3) $2\text{H}_3\text{PO}_4 + 3\text{Ca}(\text{ClO}_4)_2 + 4\text{NaOH} = 2\text{CaH}_2\text{PO}_4 + 4\text{NaClO}_4 + \text{Ca}(\text{ClO}_4)_2 + 4\text{H}_2\text{O}$
- (4) $4\text{NaClO}_4 + \text{Ca}(\text{ClO}_4)_2 + \text{Na}_2\text{CO}_3 = 6\text{NaClO}_4 + \text{CaCO}_3$

The Palmar process was designed primarily to treat low grade phosphates in regions where cheap hydroelectric power is available. While it was operated for a time in Norway with apparent success, little or none has been offered on the American market. Apart from the fact that cheap power is necessary for its commercial success, this process requires at least two and possibly three filtrations entailing either a loss of chlorate or perchlorate solution, or necessitating much washing and the subsequent evaporation of the wash water. The reagents required are probably more valuable than the product sought and while theoretically these reagents are regenerated and recovered, there is bound to be a considerable loss on account of the numerous steps involved in the process.

Miscellaneous Processes for Producing Available Phosphates.

In Table LXXVI of the Appendix, under the heading "Miscellaneous Processes" there are listed a number of patents for producing soluble and available phosphates not readily classified under other heads. Perhaps the ones which have attracted the most attention are: first, those which have to do with inoculating natural phosphates with bacteria which cause the rock to break down; and second, processes in which phosphate rock and sulfur are intimately mixed sometimes with the addition of sulfofying bacteria or composted with fertile soil and well rotted stable manure.

The fact that bacteria might increase the solubility of the phosphoric acid in bone meal seems to have been first suggested by Stoklasa⁶⁷ in 1900. Koch and Krober⁶⁸ also found that a number of relatively insoluble phosphates were rendered soluble by the acids formed by sewage and soil bacteria. A number of other investigators, notably Sackett, Patten and Brown⁶⁹ and Bassalik⁷⁰ have also reported that certain soil bacteria exert a solvent action upon mineral phosphates.

⁶⁷ Über den Einfluss der Bakterien auf die Knochenersetzung. *Centbl. Bakt.* (1900).

⁶⁸ Der Einfluss der Bodenbakterien auf das Löslichwerden der Phosphorsäure aus verschiedenen Phosphaten, *Fühling's Landwirtschaftliche Zeitung*, 7 (1906).

⁶⁹ The Solvent Action of Soil Bacteria upon the Insoluble Phosphates of Raw Bone Meal and Natural Phosphate Rock, *Mich. Agr. Expt. Sta. Special Bull.* 43, pp. 1-30 (1908).

⁷⁰ Über Silicatzerersetzung durch Bodenbakterien und Hefen, *Ztschr. Gärungsphysiol.* Bd. 3, Hft. 1, pp. 15-42 (1913).

The process of Coates⁷¹ (who has a number of patents supplementary to that for bacterized phosphate⁷²) consists in adding rock breaking down bacteria to mineral phosphates which have been sterilized by heat treatment. The bacteria it is claimed continue to act upon the phosphate rock, rendering the phosphoric acid contained therein available to crops.

The mixing of sulfur with phosphate rock to render the latter available was proposed and patented by Chisolm⁷³ in 1905 and 1906. While little was said at that time regarding the oxidation of this sulfur and the secondary effect thus produced upon the mineral phosphates, the formation of sulfuric acid in the soil by the oxidation of sulfur was noticed by Mares⁷⁴ as far back as 1869.

In 1915 Chisolm⁷⁵ took out another patent in which he claims that water soluble phosphate is obtained by intimately mixing and grinding together sulfur and phosphate rock and then introducing sufficient moisture to promote the formation of sulfuric acid.

Lipman's first patent⁷⁶ covers the mixing of sulfur and phosphate rock with soil, well rotted stable manure or other material carrying micro-organisms which tend to oxidize the sulfur present. In his two subsequent patents⁷⁷ he claims the production of a phosphate fertilizer by mixing phosphate rock, sulfur and sulfofying bacteria.

The experiments reported by Lipman, McLean and Lint⁷⁸ have shown that by composting phosphate rock and sulfur with sand or soil containing sulfofying bacteria, distinct increases in the solubility of the phosphoric acid are obtained due in a large measure to the conversion of the sulfur into sulfuric acid and the action of this acid upon the phosphate mineral. Lipman does not claim to get water-soluble phosphoric acid by this method, but citrate soluble, or so-called available phosphoric acid.

Where the phosphate rock (15 parts and sulfur (5 parts) were composted with a relatively large quantity of soil (100 parts), Lipman and Joffe⁷⁹ found over 82 per cent of the P_2O_5 was converted into a citrate soluble form in about 20 weeks. But in the experiments of Ellett and

⁷¹ U. S. Patent Nos. 947,796 (1910); 947,795 (1910).

⁷² U. S. Patent Nos. 971,830 (1910); 1,024,880 (1912).

⁷³ U. S. Patents 792,314 (1905); 824,280; 824,281 (1906).

⁷⁴ Des transformations que subit le soufre en poudre quand il est répandu sur le sol, *Compt. rend. Acad. Sci. Paris*, 69, p. 974 (1869).

⁷⁵ U. S. Patent 1,147,926 (1915).

⁷⁶ U. S. Patent 1,222,112 (1917).

⁷⁷ U. S. Patent 1,235,906 (1917); 1,361,596 (1920).

⁷⁸ The Oxidation of Sulfur in Soil as a Means of Increasing the Availability of Soil Phosphates, *Soil Science*, Vol. 1, p. 533 (1916); Sulfur Oxidation in Soils and its Effect upon the Availability of Mineral Phosphates, *Soil Science*, Vol. 2, p. 499 (1916).

⁷⁹ *Soil Science*, Vol. 10, p. 327 (1920).

Harris⁸⁰ where the amounts of soil and phosphate rock were more nearly equal (but the ratio of sulfur to rock the same as in Lipman's experiments) only about 19 per cent of the P_2O_5 present was rendered citrate soluble even after the compost heap had stood for 2 years.

A number of pot and field experiments⁸¹ have been and are being conducted with phosphate-sulfur composts and the favorable results reported indicate that this method of preparing available phosphates may be a factor in future fertilizer practice. If it should prove an effective and economic method of rendering phosphates available it would have certain advantages over the sulfuric acid process in that low grade phosphates unfit for the manufacture of acid phosphate could be readily employed. Another advantage claimed for this product is that the phosphoric acid contained therein is rendered available at a rather slow but constant rate, corresponding in a measure to the rate at which plants absorb phosphoric acid from the soil under optimum conditions.

Considerable experimentation in the laboratory and many field tests conducted for protracted periods upon a wide variety of soils are necessary before definite conclusions can be drawn concerning the relative merits of such new phosphate fertilizers and the standard carriers of phosphoric acid which have been in use for so many years.

⁸⁰ Soil Science, Vol. 10, p. 315 (1920).

⁸¹ Rumer and Tartar, Sulfur as a Fertilizer for Alfalfa in Southern Oregon, Ore. Agri. Expt. Sta. Bull. 163 (1919); Lipman and McLean, Sulfur-Phosphate Composts under Field Conditions, Soil Science, Vol. 5, pp. 243-250 (1918).

Chapter 5.

Water-Soluble Phosphates.

The most extensively used phosphates at present on the market for fertilizer purposes are those in which the phosphoric acid is in a water-soluble condition. The fact that plants draw practically all of the mineral constituents required for their normal growth from material dissolved in the soil waters makes it appear logical that water-soluble phosphates should be more quickly available to crops than those which dissolve in water to only a limited extent. It is a well known fact, however, that most of the readily soluble phosphates when applied to soils do not remain in this condition for any protracted period of time, for the bases present in the soil tend to form more basic and less soluble phosphatic compounds. Because of their water soluble condition, however, at the time of their application it is much easier to obtain a uniform distribution of such phosphatic fertilizers and even after the less soluble phosphatic compounds have been precipitated in the soil, the state of division of this reverted or precipitated material is such as to expose an immense surface to the action of the soil waters, which nearly always carry considerable quantities of carbon dioxide (the solvent power of which is well known) and thus the phosphate is more readily presented to the plant roots than that applied in so-called available but much less soluble form.

Practically all of the water-soluble phosphatic fertilizers now on the market are produced by the action of sulfuric acid upon bone or mineral phosphates. Phosphates so treated are the basis of nearly all mixed fertilizers, and thus the production of this acid is so intimately tied up with the fertilizer industry that nearly every large factory has in connection with it a sulfuric acid plant.

The sulfuric acid employed in manufacturing soluble phosphates is the ordinary "chamber acid" produced by passing the gases evolved from burning pyrites or elemental sulfur, along with air, through a system of lead chambers into which are also introduced oxides of nitrogen and water either in the form of steam or a fine spray.¹ The

¹ The manufacture of sulfuric acid has been so fully treated in a number of standard works that the writers deem it unnecessary to go into the manufacturing details.

acid thus obtained ranges in specific gravity from 1.53 to 1.71 at 60° F. (equivalent to 50° to 60° Bé), and contains from 62 to 77.5 per cent H_2SO_4 . While acid of the latter strength must be diluted before it is suitable for treating bones and mineral phosphates, it is shipped in this more concentrated form because it does not appreciably attack the ordinary steel tank cars.

TABLE XXV

SPECIFIC GRAVITIES AND THEIR EQUIVALENTS IN BAUMÉ DEGREES OF SULFURIC ACID OF VARIOUS STRENGTHS

° Bé.	Sp. Gr.	Per Cent H_2SO_4	° Bé.	Sp. Gr.	Per Cent H_2SO_4	° Bé.	Sp. Gr.	Per Cent H_2SO_4
0.....	1.0000	0.00	25.....	1.2083	28.28	49.....	1.5104	60.75
1.....	1.0069	1.02	26.....	1.2185	29.53	50.....	1.5263	62.18
2.....	1.0140	2.08	27.....	1.2288	30.79	51.....	1.5426	63.66
3.....	1.0211	3.13	28.....	1.2393	32.05	52.....	1.5591	65.13
4.....	1.0284	4.21	29.....	1.2500	33.33	53.....	1.5761	66.63
5.....	1.0357	5.28	30.....	1.2609	34.63	54.....	1.5934	68.13
6.....	1.0432	6.37	31.....	1.2719	35.93	55.....	1.6111	69.65
7.....	1.0507	7.45	32.....	1.2832	37.26	56.....	1.6292	71.17
8.....	1.0584	8.55	33.....	1.2946	38.58	57.....	1.6477	72.75
9.....	1.0662	9.66	34.....	1.3063	39.92	58.....	1.6667	74.36
10.....	1.0741	10.77	35.....	1.3182	41.27	59.....	1.6860	75.99
11.....	1.0821	11.89	36.....	1.3303	42.63	60.....	1.7059	77.67
12.....	1.0902	13.01	37.....	1.3426	43.99	61.....	1.7262	79.43
13.....	1.0985	14.13	38.....	1.3551	45.35	62.....	1.7470	81.30
14.....	1.1069	15.25	39.....	1.3679	46.72	63.....	1.7683	83.34
15.....	1.1154	16.38	40.....	1.3810	48.10	64.....	1.7901	85.66
16.....	1.1240	17.53	41.....	1.3942	49.47	64½.....	1.7957	86.33
17.....	1.1328	18.71	42.....	1.4078	50.87	64¾.....	1.8012	87.04
18.....	1.1417	19.89	43.....	1.4216	52.26	64¾.....	1.8068	87.81
19.....	1.1508	21.07	44.....	1.4356	53.66	65.....	1.8125	88.65
20.....	1.1600	22.25	45.....	1.4500	55.07	65½.....	1.8182	89.55
21.....	1.1694	23.43	46.....	1.4646	56.48	65¾.....	1.8239	90.60
22.....	1.1789	24.61	47.....	1.4796	57.90	65¾.....	1.8297	91.80
23.....	1.1885	25.81	48.....	1.4948	59.32	66.....	1.8354	93.19
24.....	1.1983	27.03						

The fertilizer trade, however, is accustomed to expressing the strength of chamber acid in terms of Baumé degrees (°Bé), therefore in the above conversion table (Table XXV), taken in part from one approved and adopted by the "Manufacturing Chemists Association" of the United States, the specific gravity of, and percentage of H_2SO_4 in sulfuric acid of various strengths are given corresponding to each degree registered by the Baumé hydrometer.

In the general process of acidulating relatively insoluble phosphates, advantage is taken of the fact that sulfuric acid being a stronger acid than phosphoric will displace the latter acid from its compounds.

In actual practice sulfuric acid is added in sufficient quantities to

combine with two-thirds of the lime present in the original mineral to form calcium sulfate or gypsum leaving one-third of the lime combined as an acid salt of phosphoric acid which is soluble in water.

ACID PHOSPHATE.

Historical.

The treatment of bones with sulfuric acid was first proposed by Liebig before the middle of the nineteenth century. In 1842 Lawes¹ took out a patent for the acidulation of bones and later when the nature of guano and phosphate rock was discovered the same treatment was applied to these materials, but while the process of acidulation increased the solubility of these materials, the product obtained in these early days was somewhat irregular in composition and often in rather poor mechanical condition.

This was due to the following causes: (1) An incomplete understanding of the action of sulfuric acid upon the various impurities occurring in natural phosphates and the consequent lack of chemical control over the raw materials entering into the manufacture of acid phosphate. (2) The limited knowledge of the importance of sulfuric acid concentration upon the rate and thoroughness of the chemical reactions and the mechanical condition of product. (3) The use of coarsely ground phosphates which were incompletely attacked by sulfuric acid. (4) The employment of hand labor in mixing the acid and rock, which made it impracticable to obtain the intimate contact necessary for rapid and complete reaction. (5) The dumping of the freshly prepared material upon open piles almost immediately after mixing, a practice which so cooled the mass that the chemical reactions were checked and the moisture content of the product was objectionably high.

A better understanding of the process of acidulating phosphates, however, soon grew up, which resulted in more economical and efficient methods being introduced. Accurately weighed charges of phosphate rock and sulfuric acid, the composition and strength of which are definitely known, have replaced the loose approximations of the early days. Fertilizer machinery for grinding, mixing, curing and disintegrating materials has reached such a high degree of perfection that there is no longer any excuse for incompletely acidulated phosphates due to improper grinding or mixing of the raw materials, nor any reason for delay in curing and shipping acid phosphate for lack of the proper mechanical facilities. But while the mechanics of this process

¹ British Patent No. 9353 (1842).

have been pretty thoroughly worked out, there still appears to be room for further chemical research. It is still reasonable to expect that a more thorough study of the action of sulfuric acid upon the various ingredients occurring in phosphate rock and a better understanding of the effect of the compounds thus produced upon the final product might lead to economies in acid consumption, a fuller utilization of our phosphate resources and a curtailment of the waste incident to the preparation of relatively pure phosphate rock.

Owing to the fact that finely ground steamed or degreased bone is generally recognized as an effective phosphatic fertilizer without further treatment, and also because water soluble phosphates can be obtained so much more readily and cheaply by the acidulation of mineral phosphates, the percentage of bone products now treated with sulfuric acid is relatively small.

In manufacturing soluble phosphates for fertilizer purposes from degelatinized bone, the bones are first ground to pass at least a 50 to 60 mesh sieve and then treated with an equal weight (approximately) of 60 per cent sulfuric acid. The mass is thoroughly mixed and allowed to stand until the chemical reactions are practically complete. Dissolved bone contains in addition to water soluble phosphate a small amount of fixed nitrogen also in an available condition, which adds to its agricultural value. The main fertilizer ingredient, however, is monocalcium phosphate and the amount of water soluble phosphoric acid (P_2O_5) in this form varies between 15 and 18 per cent, depending on the character of the bone used and the skill of the manipulator. Unfortunately the character and quantity of the organic matter in some of the bone employed is such that upon treatment with sulfuric acid a viscous mass results which is difficult to dry. This objection does not apply, however, to bone black, bone char and bone ash; all of which are used to a limited extent in the manufacture of water-soluble phosphates.

The vast bulk of the soluble phosphate produced both in this country and abroad, however, is manufactured from the amorphous phosphates of lime, the deposits of which have been previously described. The general procedure followed in making acid phosphate is a familiar one, and most of the larger manufacturers of this commodity exercise great care in its preparation,² checking both the raw materials and finished product by chemical analyses and endeavoring by the use of the most modern equipment to obtain an acid phosphate of high availability and in the best possible mechanical condition for distribution in

² Carter, S. L., American Fertilizer Handbook, Sec. D-30 (1920); Armstrong, E. H., Modern Trend in Fertilizer Plant Operation, Ind. & Eng. Chem., Vol. 15, No. 4, p. 415 (1923).

the field. Some of those engaged in the production of this material, however, have but little knowledge of the chemistry involved and are unfamiliar with the numerous details of its manufacture which are of considerable economic importance.³ Moreover, the keen competition which has sprung up in the fertilizer industry during the post war period and the tendency to progress from the old "rule of thumb" practice towards more scientific methods tends to make a thorough understanding of the chemical principles and changes involved in manufacturing this product extremely important if not essential. Phosphate rock from various sources and from different deposits in each phosphate area differs to such an extent that in order to effect the greatest economies in manufacturing acid phosphate, more complete chemical analyses than are usually demanded are often necessary and trial laboratory tests should be made in order to obtain a true index of the proper proportions of sulfuric acid and rock to employ, and the most effective concentration of acid to use. It is a well known fact that when a new grade or type of phosphate rock is shipped to an acidulating plant a considerable amount of time and material are often consumed in making up large batches or trial mixes before the proper proportions of acid and rock required to give a satisfactory product are determined.

The Mechanics of Acid Phosphate Manufacture.

The manufacture of acid phosphate involves the following four very important mechanical or physical operations:

1. The preparation or grinding of the phosphate rock for acid treatment.
2. The mixing of the finely ground phosphate with sulfuric acid.
3. The curing and drying of the acidulated material.
4. The excavation milling and bagging of the finished product.

A number of complete or self-contained units for carrying out practically all of these operations with the minimum expenditure of time and labor are now in successful operation in this country, but the majority of acid phosphate plants still conduct these various mechanical processes in a number of separate steps.

The apparatus employed and the efficiency with which these mechanical operations are conducted have a profound effect on the chemical reactions involved in the manufacture of acid phosphate and hence the perfection of grinding, mixing, handling, milling, and bagging ma-

³ Brogdon, J. S., *Amer. Fertilizer*, **39**, No. 5, p. 25; No. 6, p. 69; No. 7, p. 59 (1913).

chinery is largely responsible for the economies attained in producing this basic fertilizer ingredient.

The writers feel, therefore, that brief descriptions of the various types of machinery and equipment used in the manufacture of acid phosphate and a discussion of their functions and merits are essential for a thorough understanding of this process.

Preparation of the Rock for Acid Treatment.

The first step in the manufacture of acid phosphate is to reduce the phosphate rock to a finely divided condition so that it may be acted upon quickly and completely by the sulfuric acid. Up until about a decade ago most of the phosphate rock used for acid phosphate was ground so that 80 to 90 per cent would pass through a 60-mesh screen. Finer grinding than this was considered both unnecessary and uneconomical. The modern tendency, however, is towards a much finer product, 80 to 95 per cent through a 100 mesh screen is considered good practice. By means of modern grinding machinery and air-separating equipment this degree of fineness can be easily obtained. The use of such finely ground phosphate rock has proven economical in that appreciably less sulfuric acid is required, the reactions between the acid and mineral take place more rapidly and a higher grade product in better mechanical condition is obtained. The following table⁴ (Table XXVI), which represents the averages of several plants, serves well to illustrate this point:

TABLE XXVI

SULFURIC ACID AND RELATIVE TIME REQUIRED FOR MAKING ACID PHOSPHATE FROM ONE TON OF ROCK OF SEVERAL DEGREES OF FINENESS

Fineness Per Cent Through 100 Mesh	Sulfuric Acid Pounds of 51° Bé. Acid per Ton of Rock	Relative Time for Reaction
95.0	1,739	1.00
90.0	1,842	1.22
85.0	1,946	1.41
80.0	2,058	1.56

With fine grinding and thorough mixing of the phosphate rock with sulfuric acid the time necessary to produce a good product is reduced to a minimum. It used to be that the acid phosphate manufacturer had to let his product stand several weeks to cure before putting it on the market. The curing was necessary because the coarseness of the phosphate rock treated allowed only the surface of the larger particles to

⁴Data obtained from S. D. Kanowitz.

be acted upon immediately by the sulfuric acid and the acid permeated the layer of calcium sulfate thus formed around these particles very slowly. Long standing or "curing," however, allowed the acid to permeate deeper into rock particles and thus a higher yield of available phosphoric acid (P_2O_6) was obtained.

The extremely fine grinding now so generally adopted gives greater contact surface for the acid to act on, and allows a more thorough mixing, thus yielding a product in better mechanical condition, fully matured and ready for the market within a considerably shorter time. This means a great saving in that it is not necessary to tie up so much capital in storing the finished product.

The grinding characteristics of the different phosphate rocks vary somewhat and will be treated in a general way. The refractoriness of the rock varies not so much with respect to the phosphate mineral, but chiefly to the impurities, such as flint, sand, clays, etc., thus the Florida rocks in general are harder and more expensive to grind than the Tennessee blue and brown rocks. The pebble phosphates of Florida, however, vary considerably according to their location. For instance, those near Plant City and Lakeland are easier to grind than those near Brewster and Mulberry. As a rule, with the Florida rocks, the portion which is most difficult to pulverize is chiefly siliceous matter, while with the Tennessee brown phosphate the hardest material to grind is generally the highest in Bone Phosphate of Lime. Florida soft phosphate when dry is very easily ground, but it is never used in making acid phosphate, its chief use being for direct application to the field.

The following table, No. XXVII, prepared by S. D. Kanowitz, gives the average cost of grinding one ton of rock to 100 and 200 mesh sizes, using air separation:

TABLE XXVII

COST^a OF GRINDING ONE TON OF PHOSPHATE ROCK USING AIR SEPARATION^b

Deposits	95 Per Cent Through 100 Mesh	95 Per Cent Through 200 Mesh
Apatite (Canada)	\$0.52	\$0.91
Florida hard rock.....	.47	.83
Florida pebble (Brewster).....	.43	.75
South Carolina pebble.....	.41	.71
Idaho gray rock.....	.40	.70
Tennessee blue rock.....	.39	.68
Tennessee brown rock.....	.37	.67
Florida pebble (Lakeland).....	.37	.67
Florida soft rock.....	.33	.60

^a By S. D. Kanowitz.^b Figured on grinding 50 tons in 10 hours.

Before sending the rock to the pulverizing mills it must first be reduced to a size suitable for the mechanical operation of these mills. This is accomplished by passing the rock through a preliminary crusher, where it is broken into pieces less than an inch in diameter. There are several types of mills being used for this purpose, such as the "Swing Hammer," or "Sledge Mill," the gyratory or rotary crusher, the jaw and the roll crusher.

The hammer or sledge mill is a small machine consisting of a number of flexibly mounted rotating hammers which break up the rock and force it through spaced bars in the bottom of the mill. This type is essentially a high speed mill, and has a large capacity for its size.

The gyratory or rotary crusher works on the same principle as the household coffee mill and crushes by gradual reduction between the heavy iron cone on the rotating shaft and the chilled iron liner of the mill casing. This is a slow speed machine, but has large capacity and requires but little power to operate.

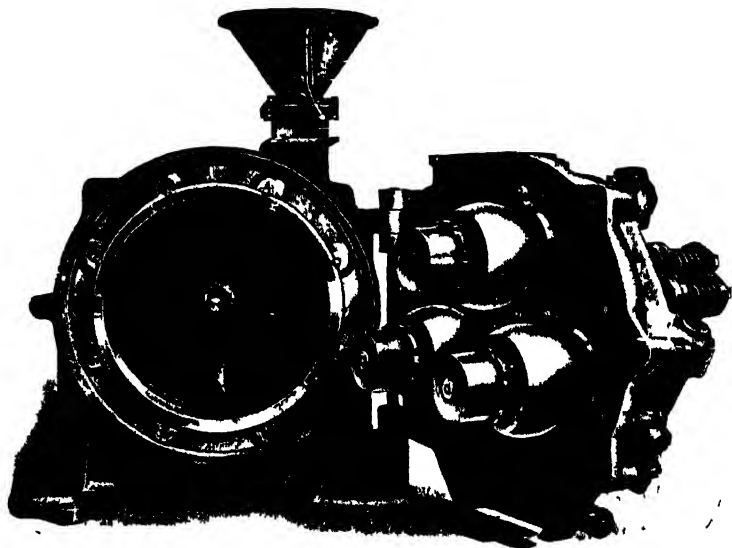
The jaw and the roll crusher is seldom used for crushing phosphate rock, so will not be discussed here.

The Florida pebble phosphates, however, require no preliminary crushing, as the lumps or pebbles are usually small enough to go directly to the pulverizing mills.

The pulverizing or fine grinding mills may be broadly grouped into three classes: first, those which depend on spring tension to hold the rolls against the grinding surface; second, those which depend upon the centrifugal force of steel rolls against a grinding face; and third, those which depend on the centrifugal force of heavy iron or steel balls rolling over each other within a cylindrical or conical shell. The methods of separating the fine from the coarse material are of two classes, namely, screen and air separation, and will be taken up along with the general discussion of the several types of mills.

The Kent and Sturtevant ring roll mills are of the spring tension type and consist of a vertically revolving concave ring against the inner surface of which three rolls are held by heavy springs. The material to be pulverized is fed to the inner surface of this ring and held there by centrifugal force while passing under the rolls. The rolls crush the material against the ring and discharge it through the bottom of the mill. From this point the crushed or ground rock is conveyed to an air separator or screening system. Screens are usually recommended for materials coarser than 60 mesh, but where the product sought is finer than this, air separation is considered more efficient. The screening system usually consists of several unit screens set at an angle of 35° to 45°, thus a comparatively coarse mesh will deliver a fine product. These screens are kept in constant vibration by numerous hammer blows

on the screen frames. (These hammers are operated either electromagnetically or by eccentric cams which raise and lower them.) This vibration keeps the meshes of the screens open and allows them to function at maximum capacity. The fine dust is then conveyed to the storage bins, while the coarse or over size is carried back to the mill by "chute" or screw conveyor to be reground. It is not desirable to use screens of a fineness below 60 to 80 meshes per inch because of the difficulty of clogging with the consequent slowing down of the screening operation. The Sturtevant mill is shown in Figure 20.



Courtesy Sturtevant Mill Co

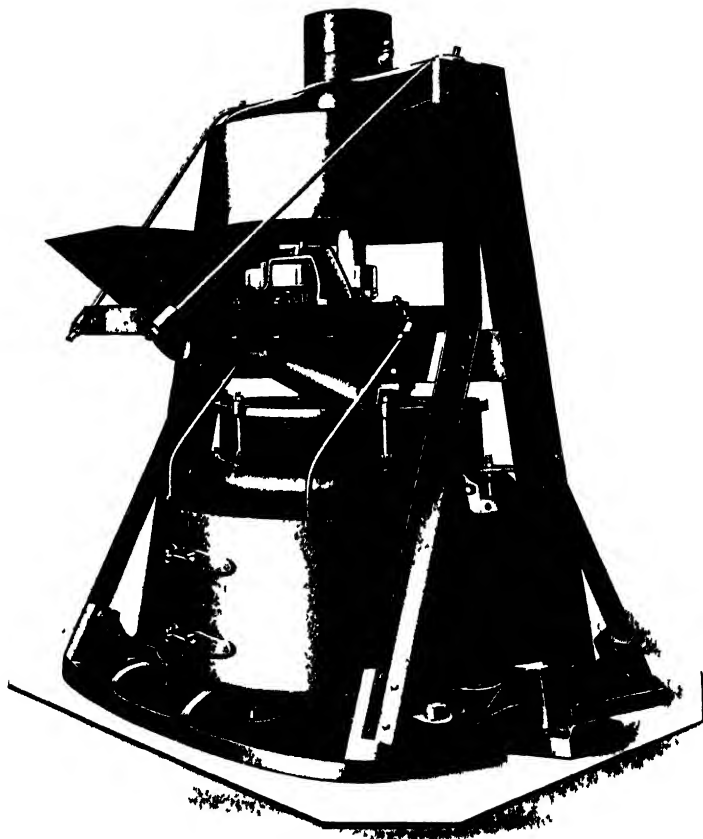
Patented

FIG 20—Sturtevant Ring Roll Mill for Grinding Phosphate Rock

There are several mills on the market which contain screens as an integral part of the mill itself.

The most widely used of this general type for grinding phosphate rock is the Bradley three-roll pulverizer, Figures 21 and 22, for which the following advantages are claimed: (1) Larger output for low power consumption, (2) Dustless in operation and low upkeep due to the few wearing parts, (3) Self-contained unit giving a finished product in one operation. Although it might appear at first sight that the small screen area in these self-contained mills would materially limit their capacity, an output of 5 to 7 tons of phosphate rock per hour, 70 to 80 per cent of which will pass a 100 mesh screen, is claimed by the

manufacturers. This degree of fineness being obtained by using a screen of 12 to 14 mesh in the mill. One criticism of the self-contained mill is the necessity of closing down when the screen becomes clogged or badly worn.

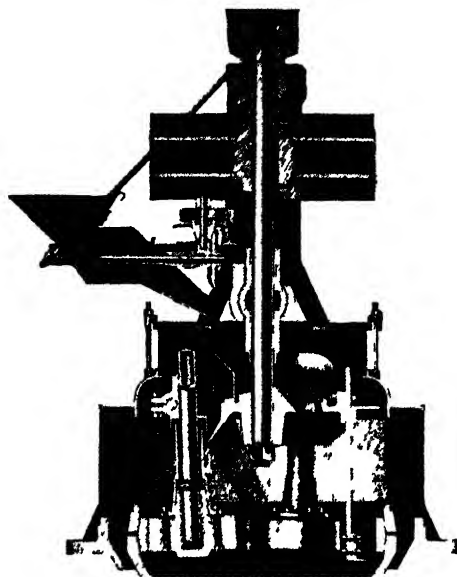


Courtesy Bradley Pulverizer Co

FIG. 21 —Bradley Ring Roll Mill Closed and Ready for Operation.

The more modern plants which have standardized on fine grinding, have equipped their mills with some system of air separation either as a part of the mill or as a separate installation. The principle of air separation is very simple and depends on the difference in dust carrying capacity of air at different velocities, thus when air is blown through a mixture of coarse and fine particles a large quantity of the fine par-

ticles are swept out and carried along at high velocity to the point where deposition is desired. At this point the air velocity is suddenly reduced by entering an expanded chamber and allowing the dust to settle. The above being the simple theory of air separation, it is now well to mention an important modification of this principle, that is, the part played by centrifugal force in obtaining uniformity of air separation where the air velocity varies to some extent. If at the point where the dust is picked up the air has a centrifugal motion the



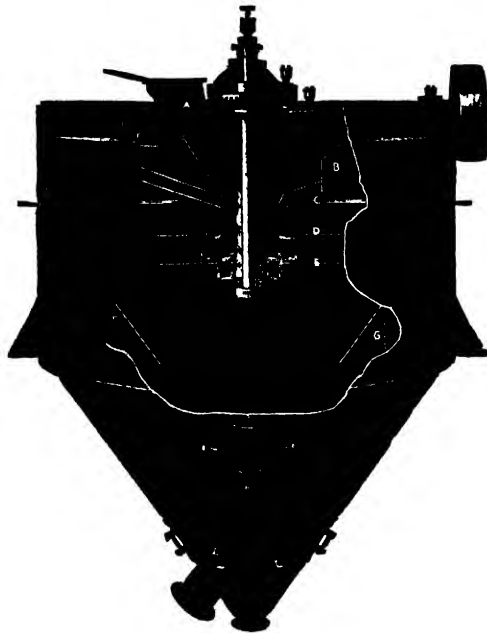
Courtesy Bradley Pulveriser Co

FIG. 22—Vertical Section of Bradley Mill Showing Internal Construction

heavier particles are thrown to the sides and go back to the mill. Now, if the air velocity is increased larger particles will be picked up, but with increase in the velocity of the air we also have an increase in the centrifugal force which throws these heavier particles to the sides, thus maintaining uniformity in size of the particles which are carried out by the air. This principle also holds true where the air velocity is reduced and proportionately smaller particles are picked up.

In the Sturtevant air separator (Figure 23) the ground material which has been conveyed from the mill by elevator is fed onto a revolving plate which distributes it in a thin stream through which a current of air passes giving a partial separation. "This product is

whirled spirally upward by the fan suction; the coarser particles being more strongly acted upon by centrifugal force, are held within an inverted conical chamber, thus being prevented from following the fines or dust, which pass upward and out with the air, through a large slow speed fan, which carries them into a second cylindrical compartment. The dust is herein again rapidly whirled by the fan blast and the increased centrifugal force thus created is sufficient to cause the



Patented

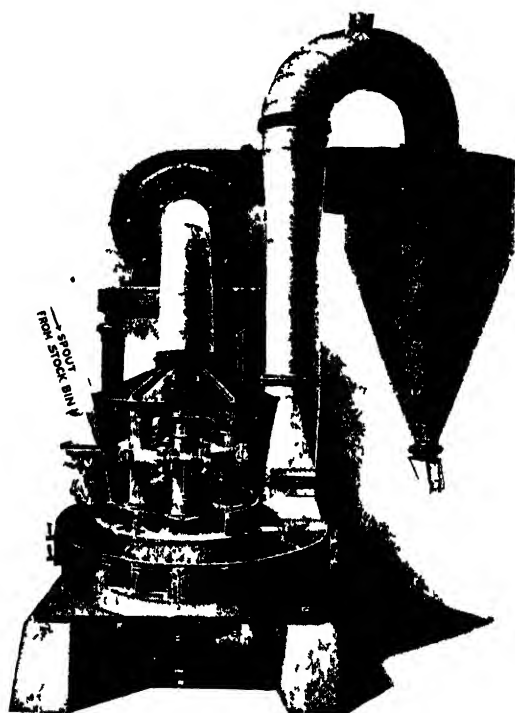
Courtesy Sturtevant Mill Co.

FIG. 23.—Sturtevant Air Separator.

fine particles to cling to the exterior walls of this chamber, gradually working spirally downward by gravity." The air from this outer cylinder returns to the inner compartment through a series of adjustable tangential vanes, thus giving an added centrifugal force to the air current. The cone hopper of the inner cylinder discharges the oversize particles which are conveyed back to the mill for regrinding. From the hopper of the outer compartment the separated phosphate dust is conveyed to the storage bins ready for acid treatment.

The second type of mill mentioned, being that which depends on centrifugal force to hold the crushing rolls against a ring or grinding

surface may be illustrated by a brief description of the Raymond mill and system of air separation (Figures 24 and 25). The material to be ground is fed to the mill by a mechanical feeder and the grinding is accomplished by suspended hard steel rolls which are forced outward by centrifugal force against a hard steel ring, the material which has passed the rolls being continually thrown up (from the bottom of the



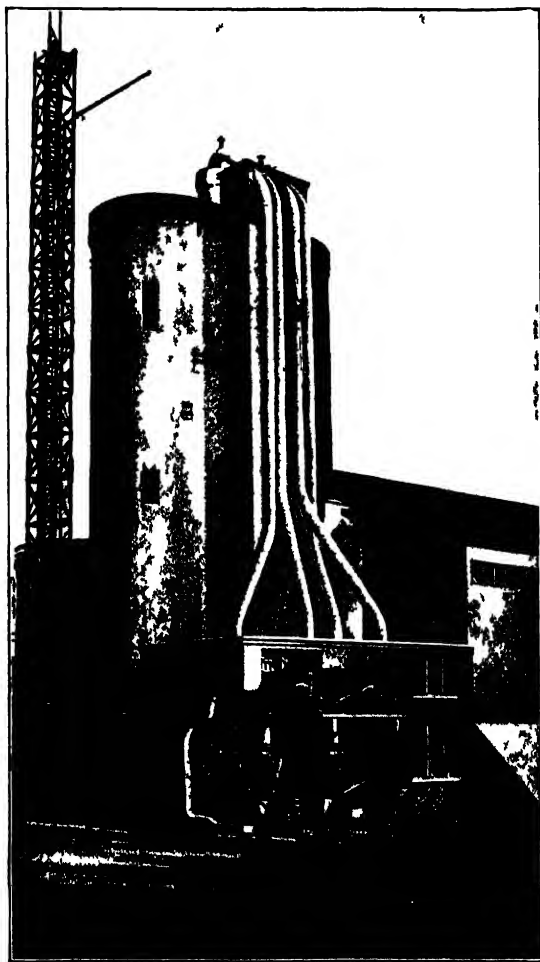
Courtesy The Raymond Bros. Impact Pul. Co.

FIG. 24—Four Roller Raymond Mill, Equipped with Air Separator

mill) between the rolls and ring by rotating plows on the lower end of the shaft which carries the rolls.

The separation of the fine from the coarse material is accomplished by means of a constant stream of air drawn through the mill by an exhaust fan. The air enters the mill at the base through openings which give a tangential or centrifugal motion to the air; passes up through rolls carrying with it the finely divided materials into the upper part of mill casing which is enlarged somewhat and acts as a separator, the heavier particles falling back into the grinding chamber. The lighter

or finely pulverized rock is carried by the current of air up through the exhaust fan and delivered to the cyclone collector which may be placed at any convenient distance away from the mill. Air and dust



Courtesy The Raymond Bros. Impact Pulverizer Co.

FIG. 25—Typical Installation of Raymond Mills and Air Separator

enter the cyclone collector tangentially and due to the extreme reduction in velocity the solid particles drop out. The air is again drawn through the mill, thus making a closed system where the grinding,

separating and transportation of the pulverized rock is done with the least possible loss.

The Hardinge conical ball mill is typical of the third type which depends on the crushing action of iron or steel balls against the walls of the rotating steel shell as well as the grinding effect of the balls rolling over each other. This mill is conical in shape and the balls employed are of hardened steel of various sizes. The large balls are



Courtesy Hardinge Co., Incorporated

FIG. 26—The Hardinge Conical Ball Mill and Air Separator.

held in the widest part of the cone by centrifugal force and naturally do the coarsest grinding. As the cone narrows to the discharge end the materials are ground more finely by the smaller sized balls. The Hardinge air separating unit (Figure 26), which has recently been put on the market, consists of a rotating drum, one end of which is connected to the discharge end of the mill and the other end to an exhaust fan which carries the dust laden air to a cyclone collector.

Due to the lower velocity of the air in this rotating drum the coarser particles of rock are here deposited. The drum is equipped with a helical conveyor and a series of lifters which pick up these coarse

particles as well as the natural discharge from the mill (including both coarse and fine rock) dropping them through the current of air which carries the finer particles to the collector. The coarser material drops into a rotating hopper which discharges into a return air pipe passing axially through the drum. The air freed from its burden of finely divided rock in the cyclone collector is returned through this pipe at a velocity sufficient to blow these coarse particles back into the mill to be reground.

The Mixing of Phosphate Rock and Sulfuric Acid.

Since the manufacture of acid phosphate is essentially a chemical process, the thorough commingling of the phosphate rock and sulfuric acid are absolutely necessary to obtain a complete reaction and the maximum yield of available P_2O_5 . Unless this mixing operation is efficiently done a considerably larger quantity of sulfuric acid may be employed than is actually required to effect the decomposition of the mineral and the product will be in poor mechanical condition and difficult to handle.

The general procedure followed is to charge simultaneously into a mechanical mixer a definite weight of finely ground phosphate and a predetermined quantity of sulfuric acid (50 degrees to 52 degrees Bé.). It is the practice of some operators, however, to charge the rock first and add the acid to the mineral while others prefer to run the acid in first and add the rock to the acid.

In the opinion of the writers the materials should be either added to the acid, otherwise the finely ground rock is apt to "ball up" and make it difficult to obtain a uniform mixture of the acid and rock within the few minutes available before the mass "sets."

There are a number of efficient mechanical agitators on the market, but nearly all of those used in the United States are of the same general type, known as the pan mixer which revolves on a vertical axis and has stirring devices which also revolve on their vertical axes within the pan but in the opposite direction to the pan.

Excellent mixers of this type are those of Stedman and Walker and Elliott. The Stedman two-ton mixer consists of a covered cast iron revolving pan 8 feet in diameter and $2\frac{1}{2}$ feet in depth capable of mixing 2 tons at each charge without danger of boiling over.

The pan is carried on ball bearings around its outer circumference and is driven by pinions at a rate of $4\frac{1}{4}$ R. P. M. The center discharge opening which is 18 inches in diameter is closed by a steel plug which fits into a renewable ring. The plug is raised by a lever which also lowers a scraper into the pan when the material is ready to be discharged.

The pan is equipped with two mechanical agitators or stirring devices which consist of heavy cast iron spiders having four arms fitted with steel plows. These stirrers are driven by bevel gears at the rate of 50 R. P. M.

The cover of the pan fits close to the revolving rim of the pan and is so constructed that the fumes evolved cannot readily escape. All parts which are apt to be worn or corroded can be readily removed and renewed.

In operating this type of mixer the weighed or measured charges of phosphate rock and sulfuric acid are run into the pan and agitated for at least 2 minutes but seldom over 3 minutes. The mass then begins to set up and it is very desirable to discharge it before it becomes so stiff that it puts an undue strain on the driving equipment and is difficult to remove entirely from the pan.

By means of a lever the plug which closes the opening in the bottom of the pan is raised, the scraping device lowered, and the material ejected either into a "den" below the mixer or into a car which hauls it to the storage shed and dumps it on a pile. The plug closing the opening in the pan is then again lowered into place, the scraper raised, and the pan is ready for another charge.

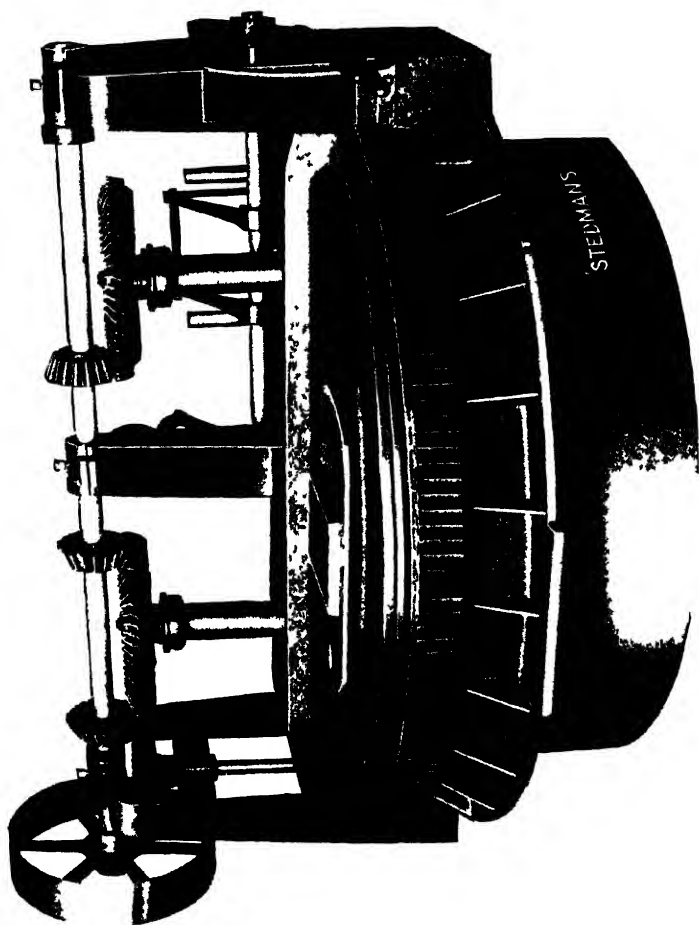
The construction of this type of mixer is shown in Figure 27.

Another type of mixer which is no longer recommended for acid phosphate and differs very materially from that just described. This machine consists of a cast iron rotatable cylinder or drum (4 feet in length and 4 feet in diameter) supported in a horizontal position and having a slot 16 inches wide running its entire length. This slot, which is the only opening in the machine, serves both to charge and discharge the mixer.

Extending through the center of the drum is a shaft fitted with stirring arms which revolves at the rate of 35 R. P. M. The whole machine is enclosed in a wooden box equipped with suitable feeding devices for the acid and rock and connected by a hopper to the acid phosphate den directly below. An exhaust pan serves to draw off the obnoxious fumes evolved during the mixing process as well as those driven off by the reactions in the den.

In operating this machine the automatically weighed charges of acid and rock are run into the mixer through the slot which is then in the upper position.

The agitating device which runs continuously as long as the mixer is in operation, is said to thoroughly mix the materials in less than two minutes. The device is then caused to rotate (at the rate of one revolution in one-half minute) and when the slot reaches the lowest position the reacting mixture is practically entirely ejected and falls by gravity



Courtesy, Stedman's Foundry & Machine Works

FIG 27—Stedman Two-Ton Acid Phosphate Mixing Pan

into the acid phosphate den where the reactions go to completion and the product is cured.

When the drum reaches its original position as shown to the operator by an indicator it is ready to be recharged.

Smaller charges (1300 pounds) were employed in this mixer than in the pan type as it was thought that more thorough agitation in a shorter period of time could be thus obtained. It was further claimed that less power was required per ton of material handled and that this mixer was practically proof against leakage during the mixing operation.

The Curing and Drying of Acid Phosphate.

During the early days of acid phosphate manufacture it was the almost universal practice to dump the material from the mixing vats directly onto an open pile where the reactions which were started in the mixer were continued and the product was cured and dried.

This method is still practiced to a limited extent in the south Atlantic States as follows:

The mixture of acid and rock is discharged from the mixer into an automatic dump car. In order that the chemical reactions may get a fair start before the mixture is discharged in a thin layer over a large open pile, it is allowed to heat up or thicken in the mixing pan; frequently it is permitted to remain in the dump car also until it has nearly set. A number of operators, however, claim to obtain good results by dumping the material almost immediately. Sometimes to prevent the acid phosphate from spreading a partly open bin is employed. The material after standing in this bin for 8 or 10 days is taken up by elevators and dumped on a storage pile.

The acid phosphate made by the open dump system naturally takes much longer to arrive at its maximum availability and optimum mechanical condition than that made by the "den" system. It is usually kept for at least one month before shipping, but adverse weather conditions may delay shipment considerably longer and even seriously affect the quality of the final product.

It is argued by those who still employ this system of curing acid phosphate that it obviates the necessity of constructing costly closed chambers and the labor and expense of digging out and rehandling the acid phosphate.

The open dump method is not, in the opinion of the writers, a satisfactory system since the heat evolved in the initial decomposition of the rock is so rapidly dissipated that the reactions may never go to completion and at best the product is imperfectly dried out. Moreover, it is impracticable to employ this system in the vicinity of large towns or in a rich farming country since with the ordinary grades of phos-

phate rock the fumes of fluorine compounds, etc., are not only obnoxious but injurious to both plant and animal life. Practically all of the larger and more progressive manufacturers of acid phosphate have abandoned the open dump method for the closed chamber or den system.

The den system was devised in order to bring about the reactions between phosphate rock and sulfuric acid in the shortest possible time and produce a pulverulent product which would require no subsequent drying.

Acid phosphate dens were originally rectangular in form and constructed almost entirely of timber. Later these dens were brick lined to give them a longer life and still later they were superseded by the cylindrical or silo type constructed of concrete and holding from 100 to 300 tons each.

In the modern acid phosphate plant several of these concrete dens are surmounted by a platform and track on which is located the mixing machinery so arranged that it can serve each den in turn. As fast as the charges of phosphate rock and acid are mixed they are dropped into one of these chambers which it is filled to within a short distance of the top. Here the chemical reactions taking place raise the temperature of the mass well above 100°C . Carbon dioxide steam and gaseous compounds of fluorine work their way out of the mass and escape through a flue at the top of the chamber, leaving the acid phosphate in a porous relatively dry condition. The material is left in the den for a period ranging from 6 to 24 hours to insure complete reaction. The top of the chamber is then removed and mechanical excavators consisting of clam shell or orange peel buckets suspended from overhead, traveling cranes pick up the acid phosphate and transfer it from the den to the storage pile for curing.

The flue through which the gases from the dens escape usually contains an exhaust fan which passes the obnoxious fumes through a series of wooden towers fitted with water sprays to decompose the silicon tetrafluoride and absorb the hydrofluosilicic acid resulting therefrom. The weak solution of hydrofluosilicic acid is employed in the manufacture of sodium fluosilicate, a compound used in the production of enamel, etc.

Acid phosphate which is carefully made, especially that produced by the den system, seldom requires any subsequent drying. It is customary abroad, however, to dry super phosphate artificially, particularly when it contains an excess of phosphoric acid or is in a poor mechanical condition due to improper mixing. There are two general methods employed in drying acid phosphate. The first consists of the application of artificial heat and the second of adding some material to take up or combine with the water or free phosphoric acid present.

In Europe a number of machines for artificially drying acid phosphate have been patented. Among the most efficient of these are the dryers of Lutjens and of Moller and Pfeiffer.⁷ In both of these machines the disintegrated acid phosphate is submitted to the action of a current of hot air under pressure. No direct heat can be used in drying acid phosphate because of the tendency of the material to revert at high temperatures.

The second method of drying acid phosphate is often practiced in this country when the material is too sticky or wet (due to faulty manipulation) to be uniformly spread on the field or mixed with other fertilizer ingredients. Such a condition when due to an excess of phosphoric acid can be frequently remedied by mixing the sticky mass with small percentages of phosphate rock or limestone. If the condition is due to the presence of a large proportion of iron and aluminum, the addition of finely ground peat or calcined gypsum will dry the material. In expelling the water from acid phosphate by artificial heating the value of the fuel consumed must be added to the cost of production, but no matter how the drying is done it entails additional handling, which is always expensive and should be avoided.

Storing, Milling, and Sacking Acid Phosphate.

In order that the acid phosphate produced may contain a maximum quantity of soluble phosphoric acid when ready for shipment, it is usually stored in well-ventilated buildings for at least two weeks. During this time the quantity of the so-called available phosphoric acid should steadily increase. This is especially true of properly mixed acid phosphate made by the "open dump" method where the heat is not sufficiently great to bring about rapid chemical reactions.

TABLE XXVIII

CHANGES TAKING PLACE IN ACID PHOSPHATE MADE FROM TENNESSEE ROCK ON STORING FROM 2½ TO 4½ MONTHS

Sample	Composition								
	Directly			After Storing for 2½ Months			After Storing for 4½ Months		
	After Mixing								
	P_2O_5		$Al_2O_3 + Fe_2O_3$	P_2O_5		$Al_2O_3 + Fe_2O_3$	P_2O_5		$Al_2O_3 + Fe_2O_3$
	Insol.	Insol.	Sol.	Insol	Insol	Sol	Insol.	Insol	Sol.
	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
A.....	2.27	1.16	2.35	1.21	0.82	2.30	1.00	1.31
B.....	2.20	1.05	1.34	2.33	1.20	1.05	2.23	1.12	1.30
C.....	1.98	1.01	1.57	2.32	1.17	1.31	2.48	1.12	1.38

⁷ Fritsch, J., *Manufacture of Chemical Manures*, pp. 123-129 (1911).

On the other hand, the storing of acid phosphate for protracted periods in large piles may impair its mechanical condition and sometimes its chemical composition. The pressure exerted on the material in the lower part of the heap, coupled with its contraction as the mass cools, tends to pack it. When the formation of gypsum is still in progress the superphosphate often becomes so closely cemented that it is difficult to break up. Again, improperly mixed acid phosphate or that high in compounds of iron and aluminum when closely packed is very apt to become gummy or to revert. Porter⁸ states that in

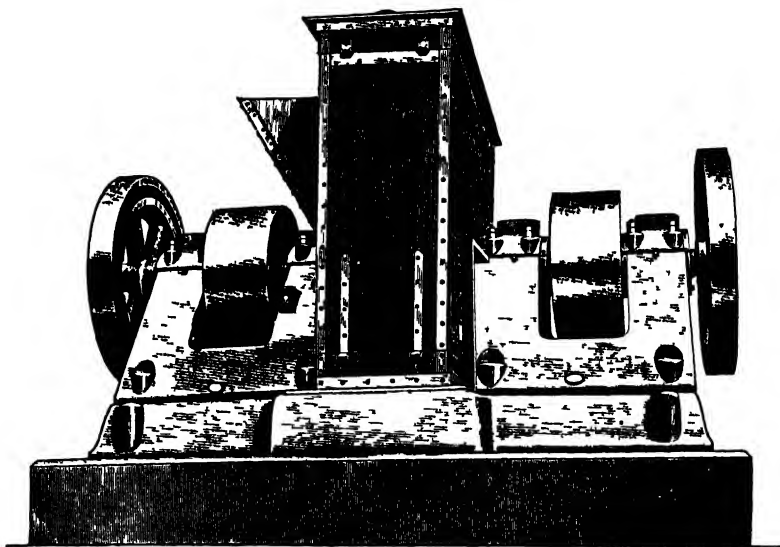


FIG. 28—Acid Phosphate Disintegrator Closed Ready for Use

making acid phosphate by the "open dump" method the material should not be discharged on the pile until it is stiff enough to "set up"

The storing of acid phosphate in medium-sized piles, however, nearly always causes trouble due to its tendency to set. Even when the material improves by storing it is hardly economical to keep it over a few months, as the interest on the money invested more than counterbalances the added value of the product due to the increase in available phosphoric acid.

In Table XXVIII, the figures of which are taken from Fritsch,⁹ the

⁸ Jour Ind Eng. Chem, 3, 108 (1911)

⁹ Manufacture of Chemical Manures, p 137 (1911)

changes taking place in stored acid phosphate made from three different samples of Tennessee phosphate (A, B, and C) are shown.

Before acid phosphate can be bagged and shipped it usually must be broken up and put through coarse sieves. In the case of superphosphate which has been carefully made and stored for a relatively short time it often suffices to throw the material against inclined screens, the force of the impact being great enough to disintegrate the lumps. When dealing with acid phosphate, however, which has been stored for a long time, it is necessary to use a machine for breaking up the material. The ordinary crushing devices do not answer for this pur-

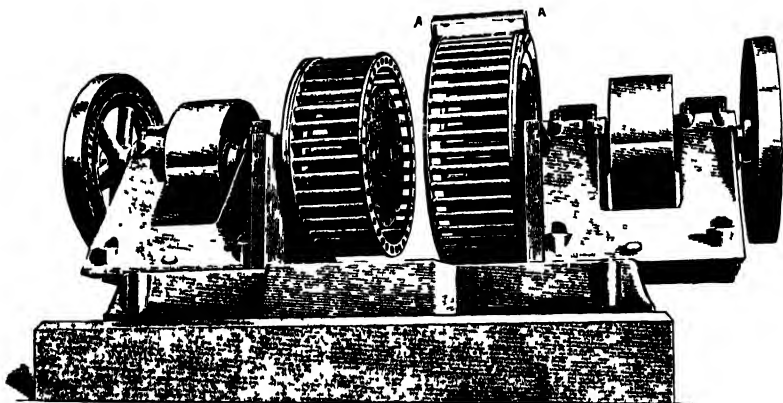


FIG. 29—Acid Phosphate Disintegrator Open to Show Construction

pose, owing to the tendency of the acid phosphate to pack or become sticky when pressure is applied, so disintegrators or mills of a special type must be employed.

In a machine like that shown in Figures 28 and 29 complete pulverization is brought about by submitting the material to innumerable shocks, but in such a manner that no opportunity is given the acid phosphate to pack or gum together.

The disintegrator consists of a number of concentric cages made up of steel bars, all of which are inclosed in a casing. The cages are usually four in number, the first and third attached to a shaft which revolves in one direction and the second and fourth attached to another shaft having the same axis but revolving in the opposite direction. The casing can be readily opened and the cages slid apart and cleaned, as shown in Figure 29.

The acid phosphate is fed through a hopper into the inner or smallest revolving cage and is thrown by centrifugal force against the

bars and into the second cage, which is revolving in the opposite direction. From the second it is thrown into the third and then into the fourth, finally being discharged from the machine thoroughly disintegrated by the numerous impacts it has received. Two scrapers fitted to the outside cage prevent the material from adhering to the casing and clogging the machine.

From the disintegrator the milled acid phosphate is taken up by ele-

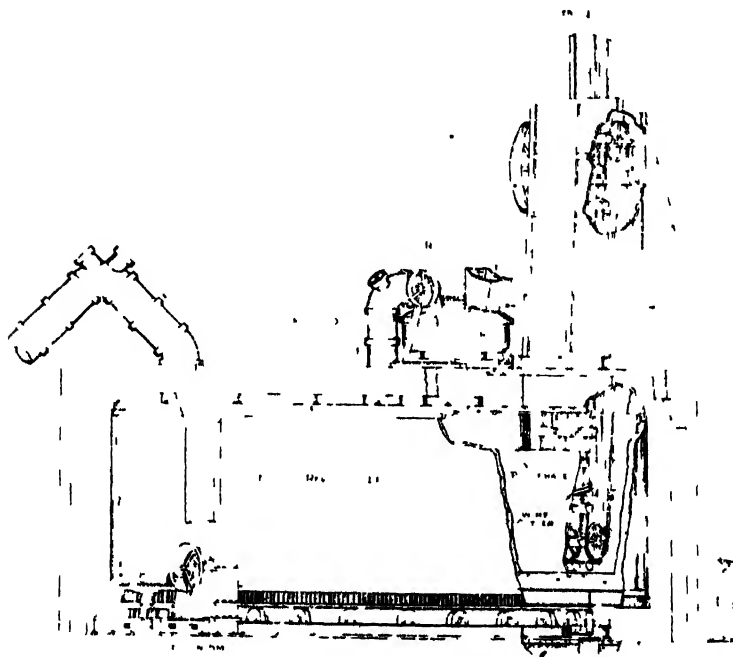


FIG. 30—Vertical Section of Forbis Revolving Den and Excavator.

vator to one or more storage bins from which it is discharged into a double weighing and sacking hopper equipped with scales and bag holders so that quick and accurate weighings may be made. The filled and weighed sacks are dropped onto a slat conveyor which carries them forward directly into the freight cars while men standing on the conveyor sew the sacks as they move.

Complete Mechanical Acid Phosphate Units.

Within the past few years a number of complete units have been invented having for their object the very rapid and in some cases the

continual manufacture, curing and conditioning of acid phosphate, thus reducing to a minimum the amount of storage space necessary in a plant having a large potential production. The three following systems which are in successful operation at a number of plants in this country are taken as typical examples of how the manufacture and conditioning of acid phosphate may be brought about in the shortest possible time.

The first type, which is known as the "Forbis Den," consists of an angular concrete den of relatively large proportions, so constructed that either the den itself or the top of the den (carrying the mixing machinery) revolves on its vertical axis. Effective means are provided to seal the joint between the den and its top, thus preventing the noxious fumes from escaping except through a flue provided for this purpose. A combined cutting device and excavator is also mounted on the platform or cover of the den, and extending down into the den, shaves off thin sections of the porous mass, elevates it and dumps it onto a storage bin or directly upon the pile for final curing. The excavator is so spaced from the mixer that it cuts and removes only the acid phosphate that has been in the den the longest period of time, the speed of the apparatus being so regulated that the material excavated is at least 8 hours old. Means are also provided for leading the fumes evolved from the mixing pan into the den and hence through a flue into an absorption or water spray system which absorbs or decomposes the noxious gases and vapors. A vertical section of this den is shown in Figure 30.

The second type designed by the Sturtevant Co. for the rapid manufacture and curing of acid phosphate is rectangular in form with wooden walls and a concrete base to which the rear wall is rigidly fastened. The side walls of this den are hinged at the top so as to allow them to swing outwardly when the den is being excavated. These side walls as well as the excavating device are suspended from a carriage which moves backward and forward upon an elevated track. The excavator, which is directly in front of this den, consists of a circular framework bolted to a vertical shaft and carrying a system of aerating fans and a series of cutting or shaving knives arranged in staggered relation to one another. The front end or door of the den is suspended by chains from a rigid superstructure, which also carries the weighing devices and the mixer for the acid and rock.

In operating this den the front door is lowered and the sides fastened at the bottom by wedges to prevent their swinging outward. The den is then filled in the usual manner with weighed charges of acid and phosphate rock which have been thoroughly stirred. After the material has set, the front door of the den is raised, the wedges removed from

the lower end of the side walls, allowing them to swing free, and the carriage from which the den walls and the excavator are suspended is moved backward by mechanical means at a slow and uniform rate, exposing the block of acid phosphate to the action of the excavator, which cuts its way into the mass, shaving off thin sections, which are at the same time aerated by the fans carried on the excavator. The disintegrated phosphate falls upon a conveyor at the side of the appa-

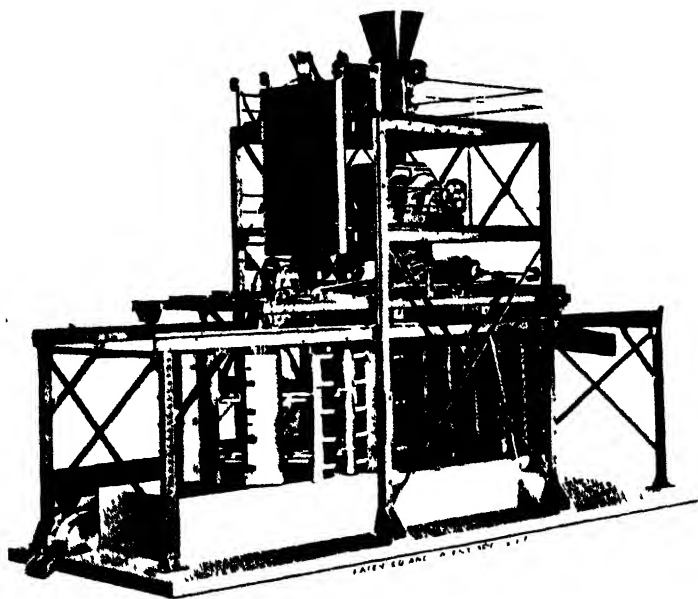


FIG. 31.—Sturtevant Complete Mechanical Unit for Manufacture of Acid Phosphate.

ratus and is carried to a pile for final curing or to the bagging machine to be sacked and shipped. This complete unit is illustrated in Figure 31.

A third system for mechanically discharging, disintegrating, and conditioning acid phosphate is known as the "Svenska" or Swedish System.

The Svenska den is rectangular in form and the front end consists of a door or gate—the full width and height of the den—which may be raised and lowered by mechanical means.

The discharging device consists of a vertical steel plate or piston which is drawn up close against the rear wall when the den is being

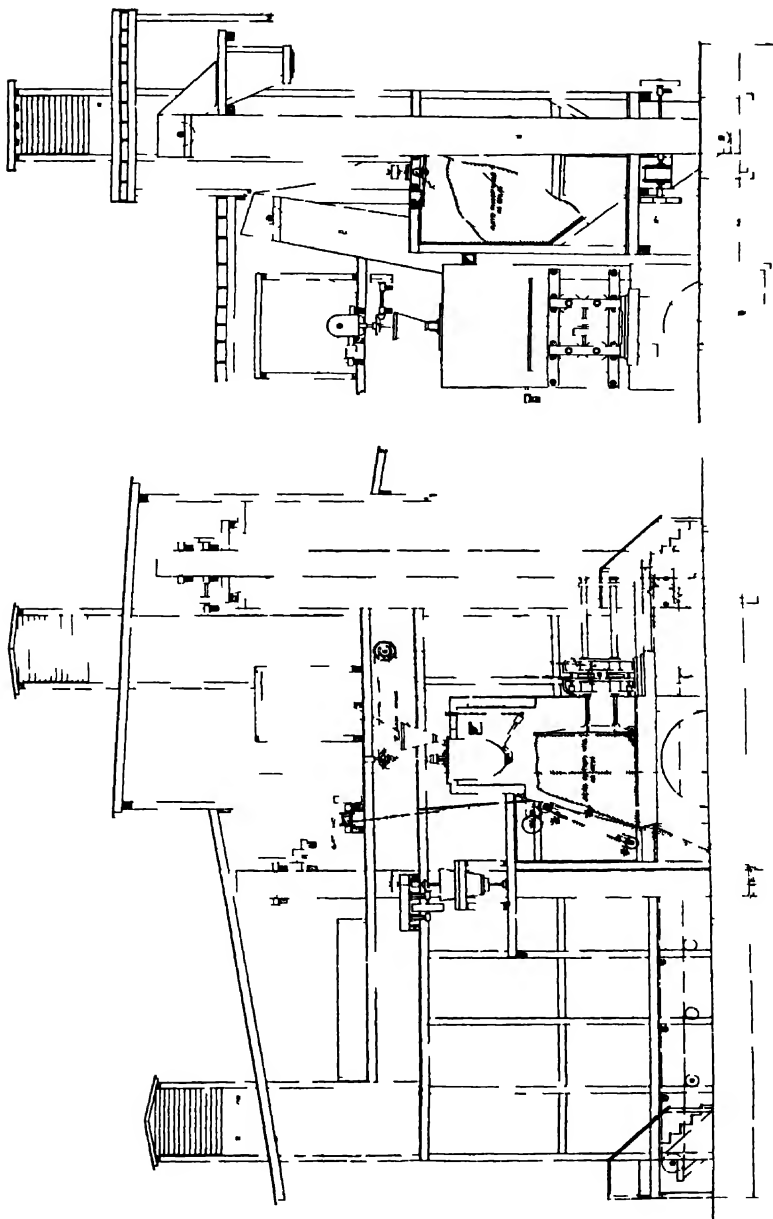


FIG 32—Side and End Views of Svenska Den System

filled, but which is pushed slowly forward by means of four mechanically operated screws when the den is ready to be discharged.

In operating this system the properly proportioned charges of phosphate rock and sulfuric acid are mixed in the usual way except that it is recommended to place the body of the mixer within the upper part of the den in order to obtain the full benefit of the heat evolved from the reacting mass of acid phosphate. The charges are dropped into the den as fast as they are mixed until the chamber is practically full. The mass is then allowed to "set" for 15 or 20 minutes, after which it is usually sufficiently firm to be removed.

The gate of the den is then raised and the discharging device or piston begins to push the block of acid phosphate slowly forward against a mechanical cutting device which crumbles or shaves the material and allows it to drop into the boot of an elevator. This elevator carries up the partly disintegrated acid phosphate and dumps it in a continuous stream into chutes which lead to a device called a rasper set into the top of a concrete silo. The rasper consists of a fan-like cutter revolving at high speed on its vertical axis. The material falling upon this device is further disintegrated and aerated, drops between the blades of the cutter and is distributed in the form of a relatively dry powder in the silo below. After remaining in the silo for approximately 12 hours it is removed and is ready for shipment. Vertical sections of the "Svenska" system are illustrated in Figure 32.

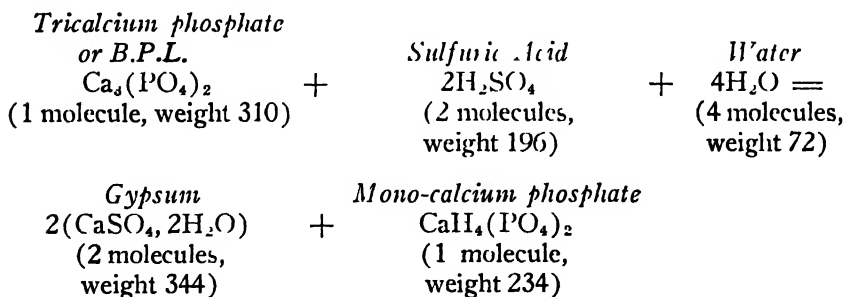
The Chemistry of Acid Phosphate Manufacture.

The four principal points sought in the manufacture of acid phosphate are: First, to obtain a product containing the maximum percentage of P_2O_5 soluble in the conventional medium (neutral ammonium citrate) designated by the American Association of Official Agricultural Chemists as a measure of the availability of phosphates. Second, the elimination of the maximum amount of moisture whereby the percentage of P_2O_5 is not only increased but the mechanical condition of the product improved. Third, the bringing about of the desired chemical reactions and the drying and conditioning of the product so it may be shipped in the least possible time. Fourth, the employment of the smallest possible amount of sulfuric acid to obtain the results enumerated above.

By the use of high-grade phosphate rock and the most up-to-date mechanical equipment the first three conditions have been satisfactorily met, but though manufacturers have expended much effort in attempting materially to reduce the amount of sulfuric acid necessary to change the phosphate into an available form they have never been entirely successful.

If phosphate rock were practically pure phosphate of lime its treatment with sulfuric acid and the preparation of a uniform product of the proper chemical composition and in good mechanical condition would offer little difficulty. But not only does the sulfuric acid added act upon the phosphate of lime, but also upon the various impurities present in the rock, such as organic matter, iron, and aluminum compounds, fluorides and carbonates, all of which consume a certain amount of acid and form products affecting the composition and physical properties of the acid phosphate. The manufacture of this product, therefore, is not as simple as many are led to believe and since the bulk of the fertilizer consumed in this country has acid phosphate as a base it is thought desirable to treat its preparation in some detail. Therefore the main reactions involved between sulfuric acid and phosphate of lime as well as the minor reactions brought about between this acid and the impurities contained in phosphate rock are described below.

Tricalcium phosphate.—It is generally assumed that phosphoric acid is combined with lime in phosphate rock to form the compound tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) known to the trade as bone phosphate of lime or B.P.L. This compound treated with sulfuric acid and water in the right proportions is converted into a mixture of gypsum and mono-calcium phosphate, this mixture being the ordinary acid phosphate of commerce. These main reactions may be quantitatively represented thus:

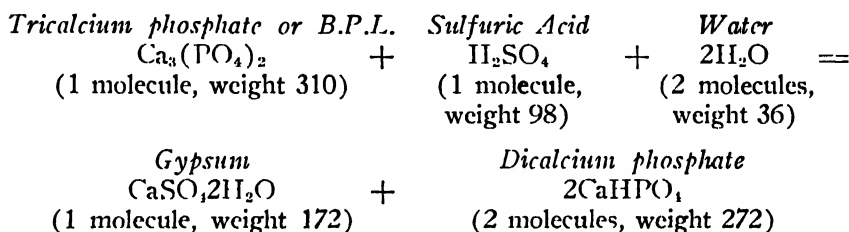


The above equation means that in order to change completely 310 parts by weight of insoluble tricalcium phosphate or *pure* phosphate rock into soluble mono-calcium phosphate and gypsum, 196 parts of pure sulfuric acid and 72 parts of water are required or 1 ton (2000 lbs.) of pure phosphate rock requires 0.63 tons of sulfuric acid and 0.23 ton of water.

Long experience in manufacturing acid phosphate, however, has shown that in actual practice better results are obtained by employing

sulfuric acid containing from 30.35 to 37.82 per cent of water (Chamber acid), (equivalent to 50° to 55° Ré.), since it is more readily mixed with the phosphate rock and gives a better product. Nearly equal quantities of phosphate rock and such acid are usually mixed and while the proportion of water in this amount of acid is about 17 per cent greater than that required to form gypsum, part of the excess is driven off by the heat of the reaction in the mass.

If less sulfuric acid is added to phosphate rock than that required to completely combine with two-thirds of the lime present, a certain amount of dicalcium phosphate is formed which though not a water soluble compound of lime and phosphoric acid dissolves readily in neutral ammonium citrate solution and is generally recognized as available to crops. This reaction may be represented thus:



In order to insure a product free from uncombined phosphoric or sulfuric acid it is customary in factory practice either to add less sulfuric acid than that theoretically required to entirely convert the lime into mono-calcium phosphate or to dust the acid phosphate product with finely ground phosphate rock or limestone. In either case a small quantity of dicalcium phosphate may be formed. Since this compound, however, answers the conventional tests for availability and full credit is allowed for such phosphoric acid in marketing acid phosphate, it would seem logical from the standpoint of economy to employ only sufficient sulfuric acid to convert the phosphoric acid of phosphate rock into the dicalcium form. With this idea apparently in mind, Hoyer-mann¹⁰ took out a patent in 1903 in which it is proposed to mix with the phosphate rock, only one-third as much sulfuric acid as is usually employed. In actual factory practice, however, this general scheme has not yet proven successful, since the resultant product nearly always consists of a mixture of water soluble, citrate soluble, and a high percentage of insoluble phosphates.

This result is accounted for by the fact that tricalcium phosphate is very readily attacked by sulfuric acid, but the tendency of the reaction is to go to an end so that either phosphoric acid or monocalcium

¹⁰ U. S. Patent No. 736,730 (1903).

phosphate is formed. While phosphoric acid is an active reagent, monocalcium phosphate has rather weak acid properties and does not readily react with the tricalcium salt. Hence phosphate rock so treated always contains a high percentage of insoluble phosphoric acid even after it has been allowed to stand for a long period of time. It is entirely feasible, however, to produce dicalcium phosphate by the treatment of acid phosphate with limestone, or burned or slaked lime, and this has often been done where a prejudice exists against soluble phosphates because of their acid properties. Such practice, however, is



FIG. 33—Interior View of Large Modern Acid Phosphate Factory

not economical since it involves additional mixing and handling and the further dilution of the final product. While considerable work has been conducted with a view to reducing the quantity of sulfuric acid necessary in producing citrate soluble phosphoric acid without much success the problem does not appear insurmountable and seems well worthy of further research.

Organic Matter.—Since practically all the phosphates with the exception of apatite, are of organic origin most of the deposits contain a certain amount of organic matter. In the case of our Western phosphates and some of the phosphate deposits of Tennessee the content of organic matter is quite appreciable. On treatment with sulfuric acid the organic matter is partially oxidized and reduces the acid to sulfur

dioxide (SO_2) and sometimes to hydrogen sulfide (H_2S). This means of course, a consumption of acid and the evolution of gases which are not only objectionable but more or less deleterious to health. The present practice, however, of drying phosphate rock either in rotary kilns or by burning it on ricks of wood oxidizes a certain amount of organic matter before the rock is acidulated. In most of the phosphate rock marketed organic matter is hardly a factor of importance, and because of the difficulty in ascertaining in just what form the organic

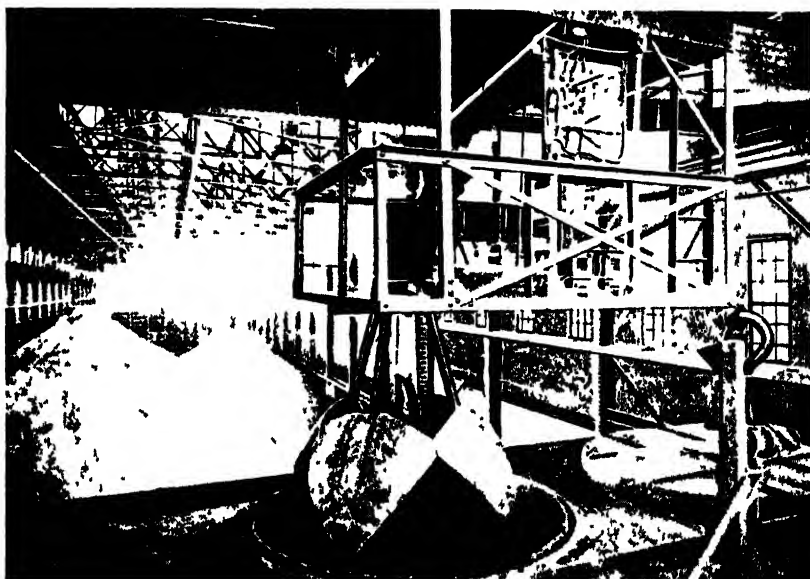


FIG. 34 --Mechanical Excavation of an Acid Phosphate Den

matter occurs it is not possible to predict what amount of acid it will consume, except by actual trial test. Little or no account is ever taken of organic matter present in the phosphate rock.

Silica and Silicates—The chief impurities found in most mineral phosphates are silica and silicates—the silica content of certain types of high grade phosphate rock running as much as 15 to 18 per cent. The presence of these impurities, however, is not considered objectionable except insofar as they dilute the mineral and render it somewhat more difficult to grind. Silica, however, plays an important rôle in the pyrolytic or volatilization method of producing phosphoric acid; in fact advantage is taken of its presence to bring about certain desired reactions and thus many phosphate deposits so high in silica as to be

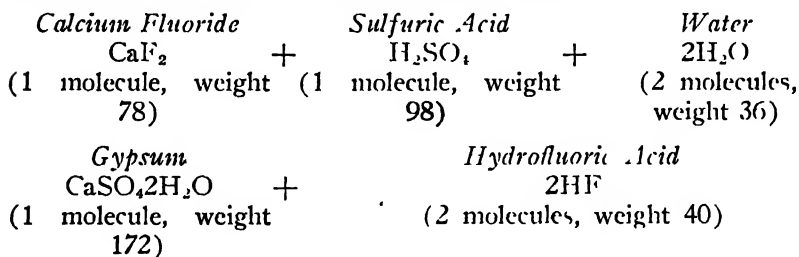
unfit for acid treatment can thus be readily utilized. The volatilization process, however, is discussed further on.

Sulfuric acid has no direct action upon silica and comparatively little effect upon most silicates, but when fluorides are present there is an indirect reaction which is described below in some detail.

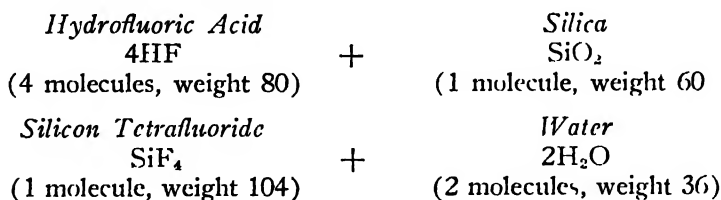
Since most silicates are acted upon to only a limited extent by sulfuric acid and this action is very slow they need not ordinarily be taken into consideration in estimating the quantity of acid required to treat phosphate rock.

Calcium fluoride.—Fluorine is present in nearly all phosphate rock, being usually combined with lime as calcium fluoride (CaF_2). In some cases the percentage of fluorine runs as high as 6 to 8 per cent, but usually not more than 3 to 5 per cent is present.

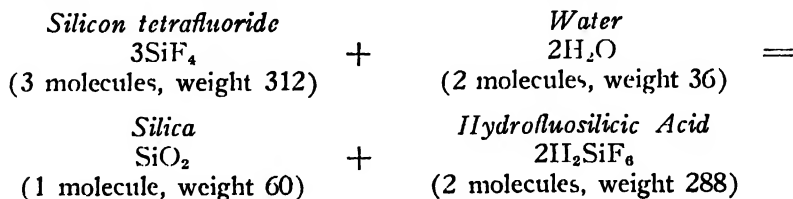
The first and main reaction taking place between calcium fluoride and sulfuric acid may be quantitatively represented thus:



A certain amount of this hydrofluoric acid (HF), however, acts upon the silica present in the rock as follows:



The silicon tetrafluoride, which is a gas, is decomposed in turn by water with the formation of silica and hydrofluosilicic acid, thus:



Before this last reaction takes place, however, a considerable amount of silicon tetrafluoride escapes as a gas and in treating mineral phosphates high in fluorides it is customary to pass the gases through spray towers or flues to decompose this compound and absorb the resulting hydrofluosilicic acid. This was done originally because these gaseous compounds of fluorine were a menace to the health of the laborers about the plant, were injurious to vegetation and a pronounced nuisance to surrounding communities. As in a number of other cases where the

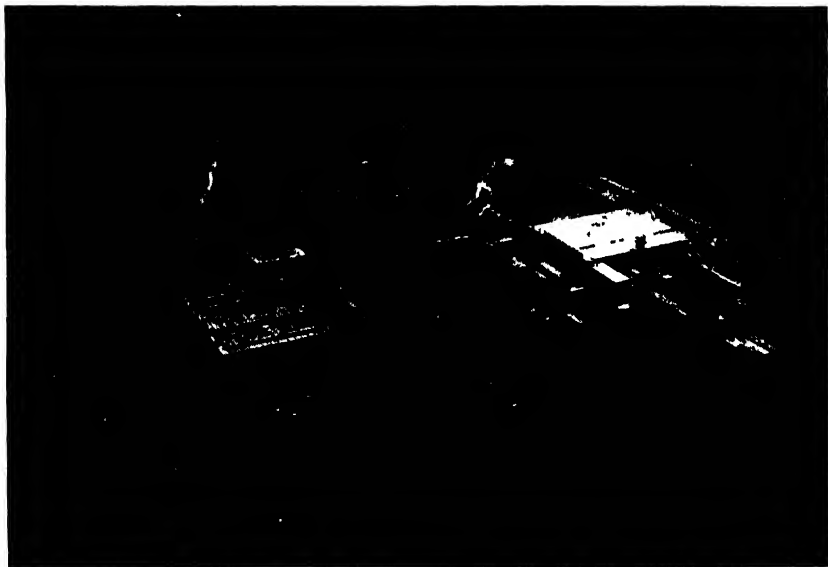


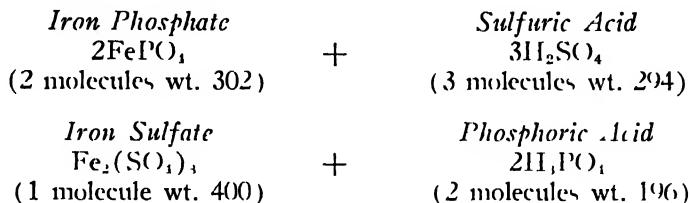
FIG. 35.—Bird's-Eye-View of World's Largest Sulphuric Acid and Acid Phosphate Plant.

abatement of a nuisance was forced upon the manufacturer, the collection of fluorine gases has resulted in the production of valuable compounds.

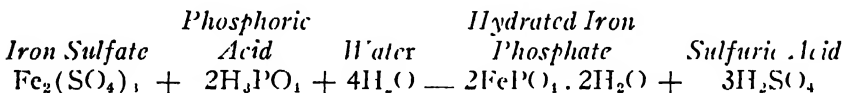
Compounds of Iron and Aluminum.—Iron and aluminum oxides, either in the free state or combined as phosphates, are the most objectionable impurities occurring in phosphate rock to be used for acid phosphate manufacture. Even when these impurities are present in relatively small quantities they cause a certain amount of "reversion" in the final product and when present in large amounts they are likely to produce a sticky acid phosphate difficult to handle and distribute uniformly in the field.

The phosphate of iron in natural occurrence may be conveniently

represented by the formula FePO_4 , although actually it may be of an indefinite composition. The exact reactions which take place when this substance is treated with sulfuric acid are not known, but unquestionably the iron is distributed between the two acids (H_3PO_4 and H_2SO_4). The general course of the reactions, however, is sufficiently well known to justify the assumption that they proceed mainly according to the following equations:



The reaction, however, indicated above is more or less reversible and in the presence of water hydrated phosphate of iron is formed as a gelatinous precipitate thus:



The hydrated iron phosphate is a very slightly soluble, sticky, disagreeable compound which if present in relatively large amounts may impart objectionable physical properties to the entire product.

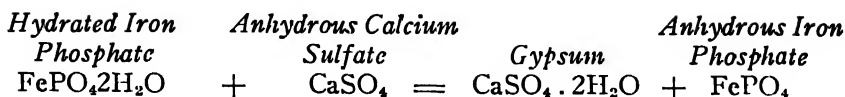
Fritsch¹¹ states that two per cent of iron oxide in phosphate rock is not objectionable because the quantity of iron sulfate produced therefrom remains unaltered in the acid phosphate, but it appears very doubtful to the writers if he is right in this assumption. It seems much more likely that the complete or nearly complete solubility of the phosphoric acid in acid phosphate made from rock high in iron and aluminum is due to the solvent effect of other compounds present, for Schneider¹² has shown experimentally that solutions of sulfate of iron increase the solubility of iron phosphate, and Cameron and Bell¹³ have demonstrated that gypsum, lime, and phosphoric acid also aid the solubility of this substance.

Hydrated iron phosphate, however, may be converted into the anhydrous and even less soluble condition by reacting with anhydrous calcium sulfate, the latter compound being converted into gypsum thus:

¹¹ Manufacture of Chemical Manures, pp. 78-79 (1911).

¹² Zeit. Anorg. Chem., 5, p. 84; 5, p. 386 (1894).

¹³ Bull. 41, Bureau of Soils.



This last reaction partly explains why acid phosphate in excellent mechanical condition but with a relatively high percentage of phosphoric acid insoluble in water is often made from rock containing large amounts of iron and aluminum. Compounds of aluminum in phosphate rock react in a manner similar to those of iron but to a less marked degree.

There is considerable difference of opinion regarding the maximum quantity of iron and aluminum which a phosphate rock may contain and still be successfully used for the manufacture of acid phosphate. Wyatt¹⁴ claims that phosphates containing from 6 to 8 per cent of iron and aluminum oxides may be used, providing there is sufficient carbonate of lime present to give a dry product. Schuecht¹⁵ and Fritsch¹⁶ seem to regard the presence of more than 3 per cent of the combined oxides of iron and aluminum as undesirable. Stillwell¹⁷ states that phosphates containing from 4 to 6 per cent of these oxides may be successfully handled but that the presence of more than 2 per cent is objectionable. In actual factory practice, however, phosphate rock containing as high as 6 per cent combined oxides of aluminum and iron are being successfully worked up into acid phosphate and though the handling of such phosphates necessitates increased care and experience, there seems little reason why they should not be employed if proper care is taken in their manipulation.

From the foregoing it would appear that in treating phosphates high in compounds of iron and aluminum great care must be exercised both in the proportioning of acid and rock, and in the subsequent curing of the product to insure the absence of excess water or acid. Probably nothing has done more towards solving this problem than the adoption of modern methods for the mechanical excavation and aeration of acid phosphate.

Carbonates of Lime and Magnesia.—The presence of carbonates in relatively small quantities is considered by some as an advantage rather than an objection in the manufacture of acid phosphate where a dry, readily handled product is of prime consideration. The carbonic acid is usually combined with lime and it is in this form that it is considered here. Sulfuric acid acts upon calcium carbonate to form calcium sulfate, water or steam and carbon dioxide. The latter escaping as a

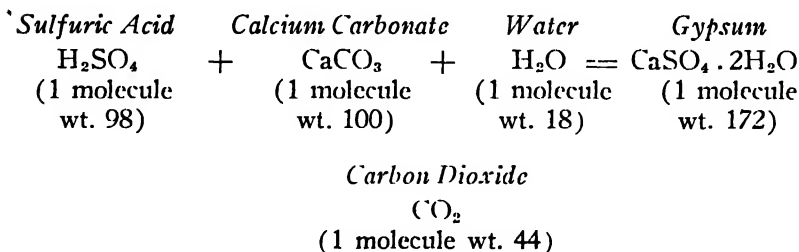
¹⁴ Phosphates of America, pp. 111-116 (1891).

¹⁵ Die Fabrikation des Superphosphates, pp. 79-83 (1909).

¹⁶ Manufacture of Chemical Manures, pp. 78-80 (1911).

¹⁷ Industrial Chem., Rogers and Aubert, p. 403 (1912).

gas, facilitates the elimination of moisture and renders the material porous and readily disintegrated. The calcium sulfate formed combines with water to form gypsum, just as in the case of the reaction between tri-calcium phosphate and sulfuric acid. The reactions may be represented thus:



In acidulating phosphates high in carbonates, the reactions begin promptly in the mixing pan because of the ease with which carbonates are acted upon by sulfuric acid. This preliminary action tends to heat the mass, which facilitates the reactions between the acid and the other constituents of the phosphate rock. The gypsum produced tends to prevent the formation of gelatinous hydrated phosphates of iron and aluminum which are so objectionable both from the physical and chemical standpoints. On the other hand, the acidulation of phosphate rock high in carbonates is not usually economical where better grades of this mineral are available, for the sulfuric acid required to decompose these carbonates adds considerably to the manufacturing cost without a corresponding increase in the value of the product. In recent years a process patented by C. G. Memminger¹⁸ has been used in the Florida phosphate fields for enriching pebble phosphate which is to be shipped abroad. This process consists of calcining the phosphate rock at a sufficiently high temperature to decompose the carbonate of lime, drive off the carbon dioxide and cause the lime to combine with silica to produce calcium silicate. In this way the actual percentage of bone phosphate of lime may be raised 3 to 4 per cent and since the calcium silicate is not readily attacked by sulfuric acid an actual saving in the cost of acidulation is thus brought about. One of the objections raised to the use of this material, however, is that the absence of carbonates causes the action between the calcined rock and sulfuric acid to be relatively slow unless the latter is heated up to give the reactions an initial impetus. The other objection is that the lack of carbonates prevents the material from becoming porous due to the escape of carbon dioxide and hence the excess of water is not so readily driven off.

¹⁸ U. S. Patent No. 1,192,545 (1916).

Quantity, Strength, and Temperature of Sulfuric Acid Required in Manufacturing Acid Phosphate.—While the quantity, strength, and temperature of sulfuric acid, which should be used in treating phosphate rock to obtain an acid phosphate containing the maximum amount of available $P_2(O)_5$ and in the best mechanical condition, cannot be determined absolutely from the chemical composition of the phosphate rock, nevertheless a close approximation may and should be made from the analysis of the phosphate which is to be acidulated.

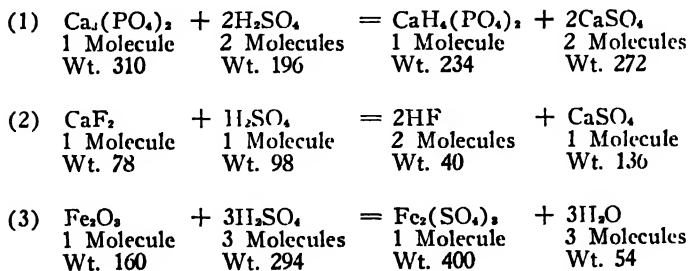
As a specific instance of how the quantity of sulfuric acid (of various strengths) required may be fairly closely determined, let us take a sample of an average grade of Florida pebble phosphate the composition of which is usually expressed in the following form (Table XXIX).

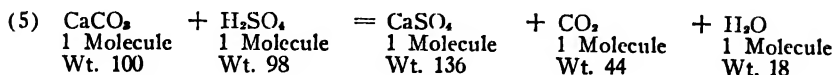
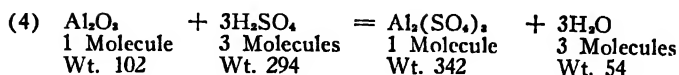
TABLE XXIX
ANALYSES OF AN AVERAGE GRADE OF FLORIDA PEBBLE PHOSPHATE

Ingredient	Composition Per Cent
Moisture	2.0
Calcium fluorides (CaF_2)	7.9
Tricalcium phosphate ($Ca_3(P(O)_4)_2$)	68.0
Calcium carbonate ($CaCO_3$)	7.5
Ferric oxide (Fe_2O_3)	1.5
Alumina (Al_2O_3)	2.1
Silica (SiO_2)	6.9
Total *	95.9

* This analysis does not include some of the minor constituents.

Since the main object in acidulating phosphate rock is to convert this phosphoric acid into an available form with due regard to the chemical action of the acid upon the other constituents in the material, the quantity of acid necessary may be approximately determined by calculating the amount required to satisfy the following equations, most of which have been previously given, but which are brought together here for the sake of clearness,





If we take the first equation shown to illustrate how the calculations are made in determining the amount of acid necessary for the treatment of this phosphate rock we see that 196 parts by weight of pure sulfuric acid are required to convert 310 parts of tricalcium phosphate into the monocalcium or soluble form. Therefore, .632 parts of acid will be required for every part of tricalcium phosphate. If we use "ordinary chamber acid" having a strength of 52° Bé. which contains according to the table on page 137, 62.8 per cent of sulfuric acid, we find that 1.016 parts by weight will be necessary for every one part of tricalcium phosphate.

In Table XXX, which is modified from one prepared by Wyatt,¹⁹ the quantity of sulfuric acid of various strengths necessary to bring about the reaction outlined above is given.

TABLE XXX

WEIGHT OF "CHAMBER ACID" OF VARIOUS STRENGTHS REQUIRED TO CONVERT ONE POUND OF EACH OF THE INGREDIENTS OF AN AVERAGE PHOSPHATE ROCK INTO THE COMPOUNDS EXISTING IN NORMAL ACID PHOSPHATE

Material Acidulated— Ingredient	Quantity and Strength of Acid Required							
	48° Bé.	49° Bé.	50° Bé.	51° Bé.	52° Bé.	53° Bé.	54° Bé.	55° Bé.
Tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$)	1.060	1.040	1.016	0.992	0.970	0.948	0.927	0.907
Calcium fluoride (CaF_2) ..	2.117	2.067	2.019	1.972	1.928	1.885	1.843	1.803
Ferric oxide (Fe_2O_3)	1.640	1.601	1.564	1.528	1.494	1.460	1.428	1.397
Alumina (Al_2O_3)	2.023	1.975	1.929	1.885	1.842	1.801	1.761	1.723
Calcium carbonate (CaCO_3)	1.652	1.613	1.576	1.539	1.504	1.471	1.438	1.407

Applying the figures given in Table XXX to the particular grade of rock under consideration it is an easy matter to determine the actual weight of acid (of each strength) required to acidulate a hundred pounds of the phosphate. These values are given in part in Table XXXI.

¹⁹ Phosphates of America, p. 110.

TABLE XXXI

QUANTITIES OF "CHAMBER ACID" REQUIRED (THEORETICALLY) TO CONVERT 100 POUNDS OF AN AVERAGE FLORIDA PEBBLE PHOSPHATE INTO ACID PHOSPHATE

Components of Rock	Per Cent Present	Strength and Quantities of Acid Required per 100 Pounds of Pebble Phosphate			
		48° Bé.	50° Bé.	52° Bé.	54° Bé.
Tricalcium phosphate ($\text{Ca}_3\text{P}_2\text{O}_8$).....	68.0	72.1	69.1	66.0	63.0
Calcium fluoride (CaF_2)	7.9	16.7	16.0	15.2	14.6
Iron oxide (Fe_2O_3)	1.5	2.5	2.4	2.2	2.1
Alumina (Al_2O_3)	2.1	4.3	4.1	3.9	3.7
Calcium carbonate (CaCO_3).....	7.5	12.4	11.8	11.3	10.8
Silica (SiO_2)	6.9
Moisture (H_2O)	2.0
Total	95.9	108.0	103.4	98.6	94.2

It can be readily seen that if the object was merely the converting of the phosphoric acid of phosphate rock into a soluble form the problem of producing acid phosphate would be a relatively simple one, but not only must the phosphoric acid be readily available but the final product should be in a mechanical condition which will admit of its ready distribution in the soil. It is customary, therefore, among manufacturers to employ somewhat less than the amount of sulfuric acid theoretically required in order to insure a dry, easily disintegrated product.

The strength of the sulfuric acid used also has an important influence on the quality of the acid phosphate. The amount of *strong* sulfuric acid theoretically necessary to produce acid phosphate is of such small bulk that it is difficult to mix it thoroughly with the ground phosphate rock; moreover, the calcium sulfate formed being less soluble in strong than in weak sulfuric acid²⁰ tends to coat the rock particles and prevent complete reaction from taking place.

On the other hand, if very dilute acid is employed the amount required for the decomposition of the rock is so large and contains such high percentages of water that the mass does not heat up readily, chemical reaction is delayed, and even if finally complete, the product contains so much moisture that it is apt to be in very poor mechanical condition. The strength of acid with which the best results are ordinarily obtained ranges between 50° Bé. and 55° Bé., although when dealing with phosphates abnormally high in iron and aluminum compounds acid of greater strength may be advantageously employed.

The temperature of sulfuric acid used also affects the quality of

²⁰ Bulletin 33, Bureau of Soils, U. S. Dept. Agriculture, pp. 41 and 42 (1906).

the acid phosphate produced, though some manufacturers pay little attention to this point, mixing their rock at all seasons with the same weight of acid at whatever the temperature of the air may happen to be. In certain localities such practice may mean a difference of 100° F. between the temperature of the acid used in summer and in the winter months. Other manufacturers believe that phosphate rock should never be mixed with sulfuric acid which has a temperature lower than 75° to 80° F., and still others use acid at 120° to 180° F. One of the fertilizer companies in this country which purchases its sulfuric acid and has it delivered at a strength of 60° Bé. dilutes this acid to 49° to 51° Bé., mixing it immediately with the ground phosphate rock, thus taking advantage of the heat generated in diluting this reagent.

While there is considerable difference of opinion regarding this point there are certain general rules which may be followed. Phosphates high in carbonates heat up quickly in the mixer and if care is not exercised, violent frothing is apt to occur and the pan overflow. It is, therefore, unwise to use highly heated acid for such phosphates. On the other hand, phosphates high in iron and aluminum compounds, and those which have been calcined to the point where the carbonates are decomposed and lime silicates formed, react very much more sluggishly and, therefore, hot acid may be advantageously employed.

No definite formulæ can be laid down which will apply to all grades of phosphate rock and no absolute rules made which will suit the different conditions under which the various factories operate. The best temperature, concentration, and quantity of acid to employ is more or less a separate problem for each individual plant and trial mixes are necessary to finally establish these points, but the manufacturer who does not exercise close supervision and chemical control over his raw materials and factory practice cannot possibly produce acid phosphate as efficiently or as economically as one who gives strict attention to such essential details.

Double Superphosphate.

Double Superphosphate, as its name implies, is a highly concentrated phosphatic fertilizer obtained as a rule by treating in two stages double the quantity of phosphate rock required for the ordinary acid phosphate. As far as its concentration is concerned, however, this product should be termed triple superphosphate since it contains about three times as much P_2O_5 as the acid phosphate produced by a single treatment of phosphate rock with sulfuric acid.

The production of double superphosphate involves first the preparation of phosphoric acid and second the use of this acid as a reagent in decomposing phosphate rock to produce monocalcium phosphate,

Since both the rock and reagent furnish P_2O_5 to the product, it is easily seen why double superphosphate carries such a high percentage of this basic fertilizer ingredient.

While theoretically the production of double acid phosphate, starting with phosphate rock and sulfuric acid is a relatively simple procedure, in actual practice it presents considerable mechanical difficulty and requires costly equipment and a large number of additional steps which partly offset the advantages gained in having a more concentrated final product.

It is necessary to use dilute sulfuric acid (27° to 30° Bé.) for the decomposition of the first batch of phosphate rock and the additional water thus introduced must be subsequently evaporated before the phosphoric acid produced can be successfully used in the treatment of the second batch of phosphate rock. The evaporation of this water adds considerably to the cost of production.

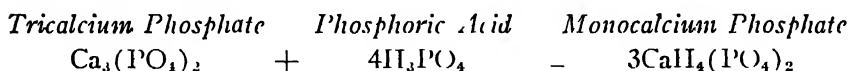
Another step necessary before the second batch of rock can be acidulated is the separation of gypsum and other insoluble impurities from the phosphoric acid. At one time this separation was effected by means of filter presses, but now the continuous counter current system of decantation has simplified this separation and phosphoric acid having a concentration of 27° to 30° Bé. can be obtained quite economically.

From the standpoints of economy and efficiency phosphoric acid appears to be the logical acid to employ in treating phosphate rock, but up to recent years when the pyrolytic methods of producing this acid were developed, phosphoric acid was only produced in commercial quantities for fertilizer purposes by the action of sulfuric acid upon bone or phosphate rock; therefore when mineral phosphates were treated with phosphoric acid it meant that sulfuric acid was being indirectly employed. But even so, the production of phosphoric acid by the sulfuric acid method and the subsequent use of this phosphoric acid to treat other batches of phosphate rock has certain advantages. In this way phosphate deposits of relatively low grade may be utilized and highly concentrated phosphate fertilizers produced which will withstand the cost of long freight hauls and heavy handling charges. The pyrolytic process of producing phosphoric acid, however, which is discussed in detail in a subsequent chapter makes it possible to produce this compound without the aid of sulfuric acid and in any desired concentration. Thus it appears that in future fertilizer practice, as well as in many other chemical operations, phosphoric acid will be very much more widely employed than in the past.

The preparation of phosphoric acid both by the sulfuric acid and pyrolytic processes is described in subsequent chapters, so only that part of the manufacture of double superphosphate involving the treatment

of phosphate rock with phosphoric acid and the curing, drying and disintegration of the product is discussed below.

Since tricalcium phosphate is the chief ingredient of phosphate rock the main reaction taking place on treating this mineral with phosphoric acid is represented thus:



While it would appear from the above reaction that the manufacture of double superphosphate is a relatively simple procedure in actual practice it requires both skill and experience. Moreover the physical properties of this product are not as desirable as those of acid phosphate and hence greater care is required in its preparation.

Just as in the case of manufacturing ordinary acid phosphate, however, the various impurities present in the mineral must be taken into consideration when figuring the proportions of acid and rock required to obtain the maximum availability of the P_2O_5 and a final product which can be readily and uniformly applied in the field.

These impurities as shown in the chapter on Acid Phosphate consist of silica, iron and aluminum oxides or phosphate calcium carbonate, calcium fluoride.

The reactions between most of these impurities of phosphate rock and phosphoric acid are quite similar to those taking place when sulfuric is employed except that the corresponding phosphate of the base is produced instead of the sulfate. The main reaction taking place when phosphate rock is treated with phosphoric acid is represented by the equation given above.

The final product is very similar to that obtained by the treatment of phosphate rock with sulfuric acid except that it is not diluted with gypsum and hence contains a much higher percentage of phosphoric acid (from 40 to 50 per cent P_2O_5) than that in ordinary acid phosphate (which contains only from 16 to 20 per cent P_2O_5).

Finally since double or triple acid phosphate contains no calcium sulfate to take up water and form gypsum, it is not, as ordinarily produced, self-drying and, therefore, is dried by artificial means. The fuel, time, and care required in reducing the moisture content also adds materially to the cost of production.

Since the sulfuric acid process of manufacturing phosphoric acid is still widely employed the most modern practice now in use is described in Chapter VI.

Treatment of Phosphate Rock with Acids Other than Sulfuric.

There are two main reasons why sulfuric acid is so universally employed in treating phosphate rock: first, it is the cheapest and most readily manufactured acid which we have and upon it we depend largely for the production of other acids, and second, because one of the products obtained by treating phosphates of lime with sulfuric acid is gypsum, which renders acid phosphate more or less a self-drying material. Other acids, however, have been proposed for this purpose, chiefly hydrochloric acid, sulfur dioxide and sulfurous acid, nitric acid, hydrofluoric acid, and phosphoric acid. In the opinion of the writers, however, only the last three warrant much consideration, but a complete list of the patented processes in which various other acids are employed is given in Table LXVI of the Appendix.

Sulfur Dioxide and Sulfurous Acid.—The use of sulfur dioxide and sulfurous acid to decompose phosphate rock has been proposed by Designolle,²¹ Bergmann,²² Machalske,²³ Meyers,²⁴ Blumenberg,²⁵ Sadtler.²⁶ If this general scheme were feasible it would simplify very much the production of soluble or available phosphates since the gases from burning sulfur or pyrites could be used directly in treating phosphate rock instead of having to go through the elaborate steps required in making sulfuric acid. Blumenberg,²⁷ moreover, claims that SO_2 does not attack the impurities of phosphate rock and hence this method offers a means of handling phosphates unsuitable for treatment with sulfuric acid.

The senior author's experience has been, however, that the weak nature of sulfurous acid renders its action upon phosphate rock very incomplete and, therefore, sulfur dioxide or sulfurous acid alone is not an efficient reagent for decomposing mineral phosphates. Meyers,²⁸ however, claims to overcome this objection by acting upon the mineral (in the presence of water) with a mixture of SO_2 , SO_3 and air, and obtains such a mixture by passing the gases from burning sulfur or pyrites through a catalyst before they come into contact with the phosphate rock.

As far as is known such processes are not in successful commercial use.

²¹ U. S. Patent No. 196,881 (1877).

²² U. S. Patent No. 852,372 (1907).

²³ U. S. Patent No. 902,425 (1908).

²⁴ U. S. Patent No. 1,246,636 (1917).

²⁵ U. S. Patent No. 1,251,741 (1918).

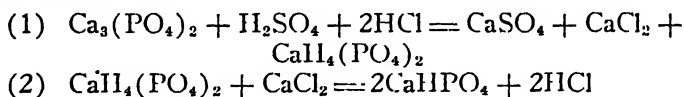
²⁶ U. S. Patent No. 1,326,533 (1919).

²⁷ Loc. cit.

²⁸ Loc. cit.

Hydrochloric Acid.—The decomposition of phosphate rock with hydrochloric acid has been suggested by Liebig,²⁹ Horsford,³⁰ Koefoed,³¹ Newberry and Barrett,³² and Glaser,³³ but unless this acid can be obtained very cheaply as a by-product of other industries it has little to recommend it. The usual method of manufacturing this acid consists in treating chlorides with sulfuric acid and under these conditions it would seem much more economical of time, money, and materials to treat phosphate rock directly with sulfuric acid. But even if hydrochloric acid can be obtained at a price which will admit of its being employed in decomposing mineral phosphates, the fact that calcium chloride is one of the products of this reaction introduces another serious objection to its use. Calcium chloride is not only very soluble in water, and therefore cannot be readily separated from the other soluble constituents in the resultant mixture, but its hygroscopic nature is such that if left in the mass it will cause the entire product to be so wet and gummy as to render it unfit for fertilizer purposes.

In order to overcome this objection and obtain a product free from calcium chloride, Newberry and Barrett³⁴ suggest treating phosphate rock with a mixture of sulfuric and hydrochloric acids, separating the solution from the insoluble residue and gypsum, evaporating the filtrate to dryness and gently igniting the dried mass. It is claimed that dicalcium (citrate soluble) phosphate is formed and hydrochloric acid driven off, collected, and used over again. The inventors represent the reactions thus:



Glaser³⁵ also proposes to precipitate and remove dicalcium phosphate from the solution obtained by treating phosphate rock with hydrochloric acid and for this purpose adds milk of lime. Calcium chloride is obtained as a by-product.

Nitric Acid.—The use of nitric acid as a reagent in effecting the decomposition of phosphate rock has been proposed by Schlutius,³⁶ Braun,³⁷ Bretteville,³⁸ and Foss.³⁹ The fact that this chemical in addi-

²⁹ U. S. Patent No. 49,831 (1865).

³⁰ U. S. Patent No. 130,298 (1872).

³¹ U. S. Patent No. 281,635 (1883).

³² U. S. Patent No. 1,020,153 (1912).

³³ U. S. Patent No. 1,235,025 (1917).

³⁴ Loc. cit.

³⁵ Loc. cit.

³⁶ U. S. Patent No. 872,757 (1907).

³⁷ U. S. Patent No. 1,058,145 (1913).

³⁸ U. S. Patent No. 1,011,909 (1911).

³⁹ U. S. Patent No. 1,292,293 (1919).

tion to its energetic acid properties brings to the product another valuable fertilizer ingredient makes it appear at first sight particularly attractive. But nitric-acid is not only an expensive reagent but because of its volatile nature and corrosive action at practically all concentrations it cannot be readily shipped from place to place like sulfuric acid. Moreover, in acidulating phosphate rock with this compound great care must be exercised that the acid used is not too strong or the temperature does not rise too high, else there will be serious losses of valuable oxides of nitrogen. The very nature of acid phosphate is such that there is a tendency to drive off any readily volatilized acid, and this is why only limited amounts of nitrate of soda and ammonium nitrate can be used in mixed fertilizers having acid phosphate as a base. In order to avoid such losses Braun⁴⁰ proposes to treat the rock with only sufficient nitric acid to produce dicalcium phosphate and thus obtain a mixture which is practically neutral, but even under the most favorable conditions nitric acid is open to the same objection as hydrochloric acid for calcium nitrate, one of the compounds formed by the reaction, is very hygroscopic and therefore likely to cause the final product to be so wet that it cannot be readily handled and distributed.

If, however, synthetic processes for producing nitric acid are so perfected that this compound can be obtained at a relatively low figure, it may at some future date play an important part in the treatment of phosphate rock. It is a significant fact that most of the patents cited above had their origin in Germany and Norway, where synthetic nitrogen compounds are being produced more cheaply than elsewhere.

Hydrofluoric Acid.—From certain standpoints the treatment of phosphate rock with hydrofluoric acid presents rather attractive possibilities. Its energetic chemical action towards silica and silicates would seem to make it ideal for enriching phosphates high in these impurities. Moreover, calcium fluoride, which is the product resulting from its reaction with certain lime compounds, is an insoluble substance which can be separated from the soluble ingredients by decantation or filtration.

On the other hand, hydrofluoric acid is not very effective in decomposing phosphates, due in part to the insoluble nature of this calcium fluoride which forms as a coating over the undecomposed phosphate, thus retarding or preventing further action by the acid. The fact also, that hydrofluoric acid is produced only incidentally in the decomposition of minerals containing relatively small amounts of fluorides as impurities makes it seem unlikely that this acid will ever be available in sufficient quantities to be a large factor in the manufacture of fertilizer.

⁴⁰ Loc. cit.

In discussing the manufacture of acid phosphate it was stated that both hydrofluoric and hydrofluosilicic acids are evolved in treating phosphates of lime with sulfuric acid, and these same products are also driven off when phosphoric acid is produced from phosphate rock by the pyrolytic process.

Hechenbleikner ⁴¹ proposes to utilize these acids of fluorine to treat another batch of phosphate rock and claims that in dilute solutions they decompose the mineral phosphates very completely. He also states that the presence of gelatinous hydrofluosilicic acid in the dilute solution causes the calcium fluoride precipitate to settle so rapidly and completely that the phosphoric acid can be readily separated by decantation. He suggests that this dilute phosphoric acid be used to reduce the concentration of sulfuric acid to the proper strength for the manufacture of acid phosphate, thus enhancing the P_2O_5 content of this product.

"Ammonium Phosphate and Concentrated Fertilizers."

Of all the compounds of phosphoric acid, those which offer the greatest promise of future expansion are the phosphates of ammonia. In fact the production of these salts bids fair to equal if not eventually outstrip that of monocalcium phosphate.

While the production of ammonium phosphates for fertilizers is growing in European countries, particularly in Germany, the use of such salts in this country has been confined largely to such minor purposes as yeast cultures, bread improvers and fire proofing compounds.

But with the great advances, which are being made in the production of synthetic ammonia and the development of the volatilization process of producing phosphoric acid, there is every reason to expect that the phosphates of ammonia will play a major part in the production of concentrated fertilizers.

Only monoammonium phosphate ($NH_4H_2PO_4$) and diammonium phosphate ($(NH_4)_2HPO_4$) are sufficiently stable compounds to be used as fertilizer materials, and even the latter compound when pure is apt to undergo some decomposition in moist air. In a dry atmosphere, however, it keeps very well and it is claimed that it can be so prepared that it will retain its ammonia under average atmospheric conditions.

With the exception of the phosphates of potash, mono and diammonium phosphate contain higher percentages of fertilizer ingredients than any other known compounds ⁴² suitable for direct application to the field. Moreover, where most fertilizer materials now on the market contain only one plant food ingredient, ammonium phosphates

⁴¹ U. S. Patent No. 1,313,379 (1919).

⁴² Monoammonium phosphate carries a total of 76.5 per cent, and diammonium phosphate a total of 79.6 per cent of combined NH_3 and P_2O_5 .

carry two—the acid and base of these salts, each furnishing a fertilizer constituent.

Two of the most widely used fertilizer materials, which carry only a single fertilizer ingredient are acid phosphate and ammonium sulfate, both of which are produced through the agency of sulfuric acid.

Acid phosphate, which has already been discussed in some detail, is a mixture of monocalcium phosphate and calcium sulfate and is manufactured by treating phosphate rock with an equal weight of 60 per cent sulfuric acid. The acid merely plays the part of a cheap reagent in this process and largely remains in the product as gypsum, which has little or no commercial value.

Ammonium sulfate, which is our chief domestic source of ammonia for fertilizer purposes is likewise produced by means of sulfuric acid. Here again sulfuric acid acts merely as a convenient means of fixing or carrying the fertilizer ingredient (ammonia) in a form, which can be readily handled and distributed.

In both these cases the acid employed has no value other than its power to convert another material into a salable form. Moreover, it acts as a diluent so that the final product contains less of the marketable ingredients than the raw materials from which they are prepared.

The substitution of phosphoric acid or sulfuric acid as an absorbent for ammonia gas is both logical and practicable. In this way the fixing power of phosphoric acid is utilized and at the same time a product is obtained, which not only possesses physical properties fully as good as ammonium sulfate, but contains high percentages of two fertilizer ingredients, which insure substantial economies in handling, shipping and distribution.

The manufacture of monoammonium phosphate is a relatively simple process and merely consists in passing the proper quantity of ammonia gas into phosphoric acid (75 per cent $\text{H}_3\text{P}\text{O}_4$). The batch heats up rapidly, then becomes pasty and finally crystallizes on cooling to a solid mass. The crystals are centrifuged to free them from mother liquor, dried and sacked. The final product is a dry, white, crystalline salt containing when pure 14.8 per cent NH_3 and 61.72 per cent P_2O_5 . It has no water of crystallization.

Pure diammonium phosphate is not as simply produced from strong acid as the mono salt since, in passing ammonia into concentrated phosphoric acid the heat of the reaction is such that the solution will no longer take up ammonia gas when a point is reached midway between, mono and diammonium phosphates. If the solution is cooled at this point the whole mass solidifies, which also prevents the absorption of sufficient ammonia to convert the product completely to the di salt.

By adding strong ammonia liquor, however, to the solution at the point where it contains approximately equal quantities of mono and diammonium phosphate, the product may be completely carried over to the latter compound. Diammonium phosphate may also be prepared by passing ammonia gas into dilute solutions of phosphoric acid, cooling and crystallizing. This entails, however, the handling of considerable mother liquor.

To insure the stability of the final product it is well to add a little less ammonia than is theoretically required, since the presence of some monoammonium phosphate tends to prevent decomposition of the diammonium phosphate.

Diammonium phosphate is also a dry nonhygroscopic, white crystalline salt containing when pure 25.8 per cent of NH_3 and 53.8 per cent of P_2O_5 , and no water of crystallization. The salt must be carefully dried at relatively low temperatures to prevent decomposition.

Ross⁴³ describes briefly an ingenious process of producing a mixture of monoammonium phosphate and monopotassium phosphate, which is being conducted on a semi-commercial scale by the Bureau of Soils at its Arlington Laboratories. This process consists in digesting potassium chloride with an excess of strong phosphoric acid in a brick lined chamber at 200°C . The potassium chloride is thus converted into potassium phosphate (KH_2PO_4) with the evolution of hydrochloric acid, which is collected as a by-product. The liquid remaining at the end of the reaction consists of a solution of potassium phosphate in phosphoric acid. The excess of acid is then taken up with ammonia and a mass of mixed crystals of ammonium and potassium phosphates obtained.

The use of more concentrated fertilizer mixtures has grown in favor during the past few years and certain standard high analysis fertilizers are recommended by agronomists and fertilizer manufacturers of twenty-four states.⁴⁴ A number of the mixed fertilizers now on the market contain twice as much plant food as some of the old standard mixtures and cannot be made up except by the use of relatively high grade materials. The manufacturer therefore is looking with increasing favor on fertilizer compounds such as ammonium and potassium phosphates and ammonium and potassium nitrates, the use of which renders it practicable to make up fertilizers of practically any desired concentration.

⁴³ The Use and Preparation of Concentrated Fertilizers, paper presented at 48th Gen'l Meeting of Amer. Electro Chem. Soc., Sept. 24 (1925).

⁴⁴ The Standard Analysis, Amer. Fertilizer, Vol. 58, No. 4, p. 27 (1923); High Analysis, Amer. Fertilizer, Vol. 59, p. 28 (1923).

Merz and Ross ⁴⁵ have applied what is known as the triangular system to the computation of fertilizer mixtures made up from such compounds as potassium nitrate, potassium phosphate and mono-ammonium phosphate, with and without the addition of lower grade materials. This convenient method of determining the possibilities and limitations of various inorganic and organic substances in making up mixed goods should be very useful to those manufacturing high analysis fertilizers and therefore a description of this system and how it is applied, both to ordinary fertilizer materials as well as to concentrated fertilizer compounds, is given below:

"Variations in the composition of mixed fertilizers may be represented by use of a system of three coördinates corresponding to the three variables, ammonia, phosphoric acid and potash. Such a system of coördinates is the triangular system, and the range of fertilizer ratios, which can be made from fertilizer materials can be readily determined with the aid of triangular section paper as represented in Figure 36."

The corners A, B, and C of the triangle represent 100 per cent of NH_3 , P_2O_5 , and K_2O , respectively. The distance from each corner of the triangle to the opposite side is divided into 100 equal parts. The sum of the distances along the respective perpendiculars, from any point within the triangle to the opposite sides, will always amount to 100 of these divisions. Each point within the triangle will therefore represent a definite mixture of all three constituents in such proportion as to total 100 per cent. Thus the point E, being 25, 50, and 25 divisions from the sides BC, CA, and AB, respectively, represents a mixture in which 25 per cent of the total fertilizing material is NH_3 , 50 per cent is P_2O_5 , and 25 per cent is K_2O . This point, therefore, represents a 25-50-25 fertilizer ratio, or any submultiple of this ratio, such as 4-8-4. Each side of the triangle represents varying mixtures of the two constituents represented by the adjacent corners, but none of that of the opposite corner. Thus the side AB represents mixtures containing varying amounts of NH_3 and P_2O_5 but no K_2O ; and the side CA varying amounts of K_2O and NH_3 but no P_2O_5 . Any particular point on a side represents a definite mixture of the two constituents represented. The point D on the side AB, for example, being 40 divisions from BC and 60 divisions from AC, corresponds to a fertilizer mixture, which contains 40 per cent of the total fertilizing elements as NH_3 , 60 per cent as P_2O_5 , and 0 per cent K_2O . * * *

A material such as sodium nitrate, in which the NH_3 amounts to 100 per cent of the fertilizing elements present, will be represented on

⁴⁵ The Computation of Fertilizer Mixtures from Concentrated Materials, Bull. 1280, U. S. Dept. Agric. (1924).

the triangle by the point A. Similarly, acid phosphate will correspond to the point B, and a potash salt to the point C. As the lines joining these three points coincide with the boundary lines of the triangle, it follows that submultiples of any fertilizer ratio, whatever may be made by combinations of these three materials. The maximum fertilizer

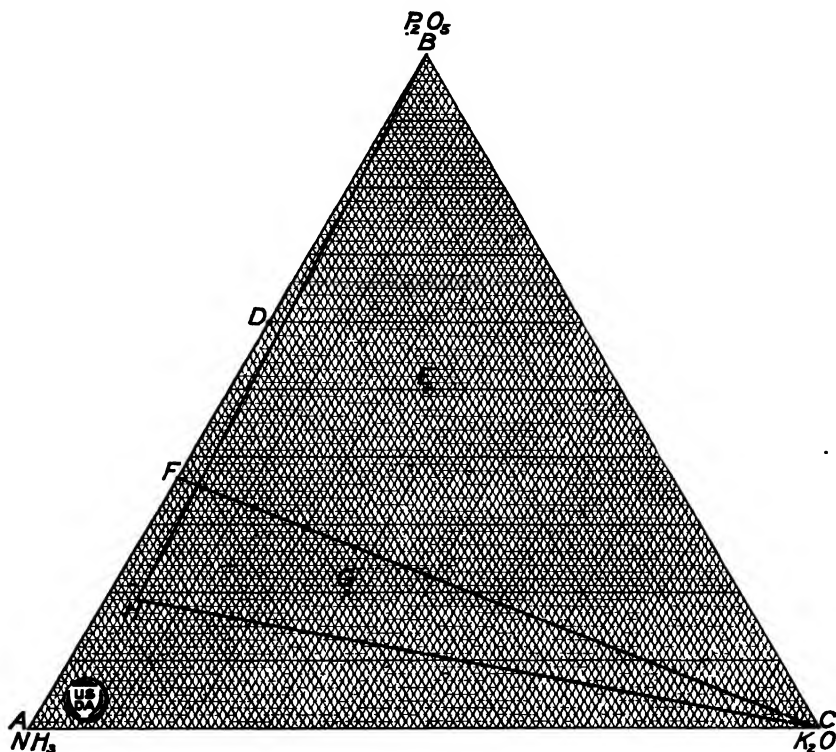


FIG. 36.—Triangular Diagram Illustrating Graphical Representation of Fertilizer Ratios.

analysis formula possible for any given ratio is obtained by multiplying by the factor $\frac{2000}{X + Y + Z}$. Thus, if the sodium nitrate contains 18 per cent NH_3 , the acid phosphate 16 per cent P_2O_5 and the potash salt 20 per cent K_2O ; then, for a 4-8-4 mixture, $X = 444$, $Y = 1000$, $Z = 400$, and $X + Y + Z = 1844$. The maximum possible analysis formula, corresponding to the mixture 4-8-4, that can be made from these materials is, therefore $\left[\frac{2000}{1844} (4-8-4) \right]$ or 4.34-8.68-4.34.

A material, for example a tankage containing, say, 8.5 per cent NH_3 and 5 per cent P_2O_5 , would have 63 per cent of its fertilizing elements in the form of NH_3 and 37 per cent as P_2O_5 , and would be represented in the triangle on the side A B by the point F. Submultiples of all ratios which fall within the triangle F C B can therefore be made from this material in combination with acid phosphate, and a potash salt, while those which fall outside this triangle, such as the analysis formula 5-2-3 corresponding to the ratio 50-20-30 represented by the point G, cannot be made. G, however, falls within the triangle F C A, and, therefore, submultiples of the ratio 50-20-30 can be obtained by combinations of tankage and potash salt with a nitrogenous material.

If one half of the ammonia in a 4-8-4 fertilizer mixture is to be obtained from nitrate of soda, one fourth from cottonseed meal, and one fourth from tankage, then 2 of a total of 4 parts of NH_3 will be present in the mixture as nitrate, 1 as cottonseed meal, and 1 as tankage. But the quantities of the two last materials, which contain 1 part each of NH_3 , also contain 0.96 part of P_2O_5 and 0.23 part of K_2O . The mixture of these three materials therefore contains 77 per cent of the fertilizer constituents as NH_3 , 19 per cent as P_2O_5 , and 4 per cent as K_2O and may be represented in Figure 36 by the point II. Submultiples of all ratios, which fall within the triangle II B C can be made by combinations of these three materials with acid phosphate and a potash salt. The maximum fertilizer analysis formula that can be made of any of these ratios is obtained in the usual way, by multiplying by the fraction

2000

$$\frac{2000}{X + X' + X'' + Y + Z}$$

The concentrated materials, monoammonium phosphate, monopotassium phosphate, and potassium nitrate, contain combinations of all three fertilizer constituents in groups of two, and all have chemical and physical properties, which make them admirably suited for use in fertilizers. Potassium nitrate has long been used to a limited extent in fertilizers, and is obtained from Chilean nitrate and other sources. It may also be prepared by treating potassium chloride with nitric acid, such as that produced in the fixation of nitrogen. Monoammonium phosphate is now being used to some extent in high-grade fertilizers, and may be prepared by neutralizing ammonia, such as obtained in the fixation of nitrogen, with phosphoric acid. The use of monopotassium phosphate in fertilizers has been limited to experimental tests only. It may be prepared from potassium chloride and phosphoric acid. The percentage composition of these salts is given in Table XXXII.

TABLE XXXII

Salt	Composition on Basis of—					
	Total Material			Fertilizing Elements Present		
	NH ₃	P ₂ O ₅	K ₂ O	NH ₃	P ₂ O ₅	K ₂ O
Monoammonium phosphate, NH ₄ H ₂ PO ₄	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
Monopotassium phosphate, KH ₂ PO ₄	14.80	61.72	19.34	80.66
Potassium nitrate, KNO ₃	16.85	46.58	26.57	74.43

Applying the triangular system to fertilizer mixtures from concentrated materials, it is seen from the percentage values given in Table XXXII that monoammonium phosphate corresponds to the point D in the triangle of Figure 36; monopotassium phosphate to the point E and potassium nitrate to the point F. These three materials may therefore be used to make submultiples of all fertilizer ratios falling within the triangle DEF. In the same way, triangles may be drawn corresponding to combinations of any two of these compounds with a nitrogen, phosphoric acid, or potash salt. Thus the triangle ADE incloses all possible ratios that can be made with mixtures of monoammonium phosphate, monopotassium phosphate, and a nitrogen compound; the triangle CDE all ratios that can be prepared from the same two compounds and a potash salt, and the triangle BDE all the ratios that can be made from these two compounds and a phosphatic material, such as acid phosphate.

When each of three materials selected for a mixture contains two fertilizing elements, then the amount of each required to give a ton of a fertilizer of any analysis formula, which they are capable of making, as shown by the triangle method, may be calculated as follows:

If A, B, and C are the percentages respectively of the NH₃, P₂O₅, and K₂O desired in the mixed fertilizer, and—

X = Weight of material containing a per cent NH₃, and b per cent P₂O₅.

Y = Weight of material containing b' per cent P₂O₅, and c per cent K₂O.

Z = Weight of material containing c' per cent K₂O, and a' per cent NH₃.

$$\text{Then } X = \frac{2000b'c'A + a'cB - a'b'C}{ab'c' + a'bc} \quad (1)$$

$$Y = \frac{2000B - bX}{b'}, \text{ and} \quad (2)$$

$$Z = \frac{2000C - cY}{c'} \quad (3)$$

For the particular case where the three materials used are monoammonium phosphate, monopotassium phosphate, and potassium nitrate respectively,

$$X, \text{ monoammonium phosphate} = 2000 \frac{2430.54A + 582.84B - 879.23C}{71945}$$

$$Y, \text{ monopotassium phosphate} = \frac{2000B - 61.72X}{52.18}$$

$$Z, \text{ potassium nitrate} = \frac{2000C - 34.6Y}{46.58}$$

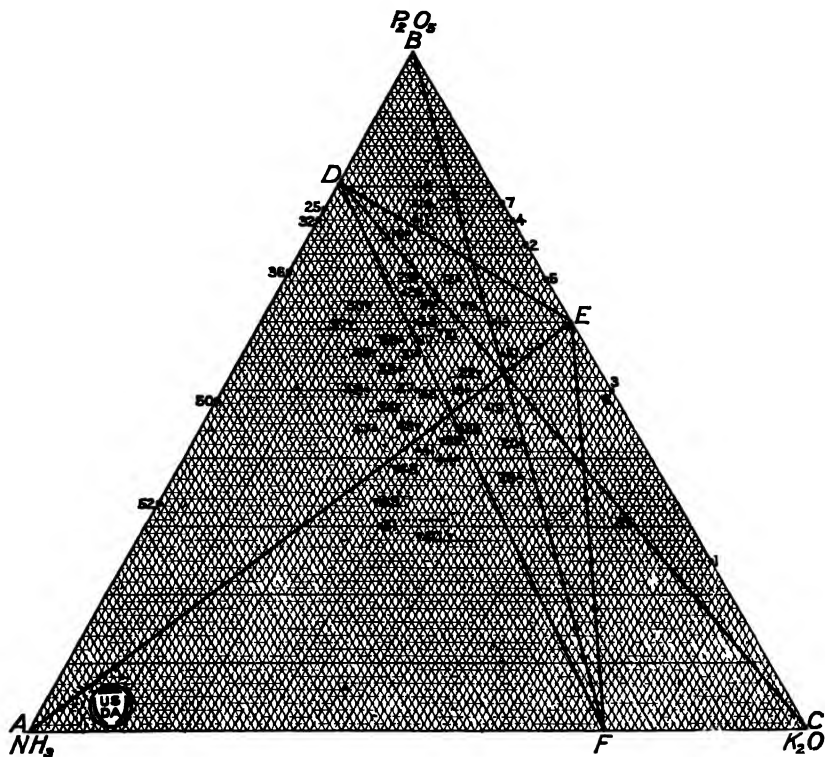


FIG. 37—Triangular Diagram Showing Fertilizer Ratios Obtainable from Concentrated Fertilizer Salts.

The number of fertilizer ratios it is possible to make from these materials is limited, as already explained, and the same is true of any three materials which contain two constituents each. However, by successively combining these materials in pairs with ammonia, phosphoric

TABLE XXXIII

EXPRESSIONS FOR CALCULATING THE QUANTITIES OF MATERIAL REQUIRED FOR A TON OF AN A-B-C FERTILIZER WHEN MATERIALS THAT CONTAIN TWO FERTILIZING ELEMENTS ARE COMBINED IN PAIRS WITH AN NH_3 , P_2O_5 , OR K_2O SALT

Mixture of—	X	Y	Z	M_{NH_3}	$\text{M}_{\text{K}_2\text{O}}$	$\text{M}_{\text{P}_2\text{O}_5}$
$X + Y + \text{M}_{\text{K}_2\text{O}}$	$\frac{2,000 A}{a}$	$\frac{2,000 B-b X}{b'}$	$\frac{2,000 C-c Y}{c''}$	
$X + Y + \text{M}_{\text{NH}_3}$	$\frac{2,000 B-b' Y}{b}$	$\frac{2,000 C}{c}$	$\frac{2,000 A-a X}{a''}$	
$X + Y + \text{M}_{\text{P}_2\text{O}_5}$	$\frac{2,000 A}{a}$	$\frac{2,000 C}{c}$	$\frac{2,000 B-b X-b' Y}{b''}$
$Y + Z + \text{M}_{\text{NH}_3}$	$\frac{2,000 B}{b'}$	$\frac{2,000 C-c Y}{c'}$	$\frac{2,000 A-a' Z}{a''}$	
$Y + Z + \text{M}_{\text{P}_2\text{O}_5}$	$\frac{2,000 C-c Z}{c}$	$\frac{2,000 A}{a'}$	$\frac{2,000 B-b' Y}{b''}$
$Y + Z + \text{M}_{\text{K}_2\text{O}}$	$\frac{2,000 B}{b'}$	$\frac{2,000 A}{a'}$	$\frac{2,000 C-c Y-c' Z}{c''}$	
$Z + X + \text{M}_{\text{K}_2\text{O}}$	$\frac{2,000 B}{b}$	$\frac{2,000 A-a X}{a'}$	$\frac{2,000 C-c' Z}{c''}$	
$Z + X + \text{M}_{\text{NH}_3}$	$\frac{2,000 B}{b}$	$\frac{2,000 C}{c'}$	$\frac{2,000 A-a' Z-a X}{a''}$	
$Z + X + \text{M}_{\text{P}_2\text{O}_5}$	$\frac{2,000 A-a' Z}{a}$	$\frac{2,000 C}{c'}$	$\frac{2,000 B-b X}{b''}$

X, quantity of material containing a per cent NH_3 , and b per cent P_2O_5 .

Y, quantity of material containing b' per cent P_2O_5 , and c per cent K_2O .

Z, quantity of material containing c' per cent K_2O and a' per cent NH_3 .

M_{NH_3} , quantity of material containing a'' per cent NH_3 .

$\text{M}_{\text{P}_2\text{O}_5}$, quantity of material containing b'' per cent P_2O_5 .

$\text{M}_{\text{K}_2\text{O}}$, quantity of material containing c'' per cent K_2O .

acid, and potash salts, nine possible combinations are obtained and can be used, by varying the materials in any combination, to make any fertilizer ratio whatever. In Table XXXIII are given expressions for calculating for each of these nine combinations, the quantities of the materials required for any fertilizer formula falling within the triangle, representing the combination in Figure 37.

For further details concerning the computation of fertilizer mixtures, conforming to the 52 analyses adopted by conferences of agronomists and fertilizer manufacturers as standard for 24 states, the reader is referred to the original article of Merz and Ross.⁴⁶

⁴⁶ Loc. cit.

Chapter 6.

The Manufacture of Phosphoric Acid by the Sulfuric Acid Process.

The production of phosphoric acid on a large scale by the sulfuric acid process was originally undertaken with a view to utilizing lower grades of phosphate rock which yielded only relatively dilute acid phosphate.

The plan suggested was to treat such phosphates with sufficient sulfuric acid to convert completely their P_2O_5 content into orthophosphoric acid, filter off the insoluble residue, evaporate the phosphoric acid and use this strong acid solution to treat a second batch of phosphate rock, producing thereby the concentrated fertilizer material commonly known as double superphosphate, the manufacture of which has been previously described.

When the higher grade phosphate deposits of the United States were discovered the preparation of phosphoric acid as an intermediate product in the manufacture of phosphatic fertilizers was no longer essential.

Fritsch ¹ in 1916 stated that "the production of phosphoric acid has lost much of its former importance." But he was evidently referring to its use in the production of fertilizers in European countries, for at no time has it appreciably declined in the United States. Moreover, the conditions today in this country are such that the manufacture of this acid for fertilizer, food and technical purposes is an immense industry and one which is growing more important each year.

Large quantities of phosphoric acid are being used in the manufacture of double or triple superphosphate, in the production of monocalcium and sodium phosphates for baking powder purposes, and for the production of phosphate water softeners. Smaller but appreciable quantities are employed in the production of yeast cultures, in soft drinks, in sugar refining and in rust proofing and fire proofing compounds. In addition to its use for the prime purpose of making phosphates, there appears to be an attractive possibility of employing this acid as a reagent in certain industrial processes instead of sulfuric acid

¹ Manufacture of Chemical Manures, p. 151 (1916).

and thus obtain a product or by-product of commercial value. This use, however, would apply chiefly to the phosphoric acid produced by the volatilization or pyrolytic process wherein no sulfuric acid is involved in its preparation.

The old process of producing phosphoric acid by means of sulfuric acid consists in first treating the phosphate rock or bone with sulfuric acid of 30° Bé. and then passing the solution through a series of filter beds or presses to remove the undissolved and precipitated material.

If the solution of phosphoric acid (28° to 30° Bé.) thus obtained is to be used for the manufacture of fertilizer it may be sent direct to the evaporators, but if it is to be employed to produce food grade acid or acid for the chemical trades it must be put through a purification process, the details of which are discussed in a subsequent chapter.

In order to obtain a good yield of acid by this process it is necessary to wash the residue on the filter beds or in the presses with considerable quantities of water resulting in the production of large volumes of weak phosphoric acid. The process, however, is a cyclic one since this weak liquor is reintroduced into the system as a diluent for the sulfuric acid employed in treating the next batch of phosphate rock or bone.

The main disadvantages of this old process lie in the facts that the filter beds or presses become clogged, filtration is slow, excessive quantities of water must often be employed in washing the residue and the filters must be continually cleaned and frequently repaired because of the corrosive action of the acid on almost all filtering media.

The following description by Fritsch² of the manufacture of phosphoric acid (from low grade rock) for fertilizer purposes is typical of the process as practised before the introduction of more modern methods.

"The ground phosphate is fed into the vats by a chain elevator 1 to 2 tons per charge; the sulfuric acid and necessary water (wash water containing P_2O_5) to dilute the acid to 16° Bé., is run in at the same time. The charging of the vats lasts twenty minutes, and during this time decomposition is completely effected,³ the phosphoric acid is liberated, the sulfuric acid has taken its place and combined with the lime to form gypsum, which has to be separated from the liquid. For this purpose the muddy liquids from the decomposition vats are collected in a collecting tank lower down, fitted with an agitator, its rôle is to maintain the solid particles in suspension until the mixture is forced to the filter presses by a membrane pump, in which the acid liquid alone comes in contact with rubber or lead. The filter presses used

² *Manufacture of Chemical Manures*, p. 152 (1916).

³ The time given by Fritsch as necessary for complete decomposition of the rock is hardly long enough.

have 50 plates, and are capable of treating 14 tons of phosphate in 24 hours. The filter plates are of pitch pine, the frames of the same wood or of oak. The gutters are of plum tree wood. When the filter press is charged, its contents are washed with water under pressure until the liquid which flows away only tests 0.25° Bé., a density equal to that of gypsum saturated water. The wash water then contains on an average 3 per cent of P_2O_5 ; it is used as already seen to reduce the sulfuric acid to 16° Bé. The phosphoric acid collected in a weak solution tests about 12° Bé. or about 4° Bé. less than the sulfuric acid used.

It was first attempted to concentrate the acid by lead coils, but the pipes became rapidly incrustated with lead salts and lost their conductivity. This process was therefore abandoned⁴ and attempts made to concentrate the acid by bottom heat. Great flame ovens were constructed heated by combustion gases. These gases are led underneath the liquid contained in a pan surmounted by an arch, the pan is of wrought-iron lined with stones which resist acid, and thus was protected from direct contact with the flame and the phosphoric acid. (On the other hand, the exterior of the pan is naked. The dilute solution of phosphoric acid runs in continuously in the back part of the pan until after two or three days an average concentration of 50° Bé. is obtained."

Although the procedure as described by Fritsch is in a general way correct, American practise differs considerably in detail. For instance, instead of filter presses, filter beds having perforated acid resisting metal bottoms covered with burlap are usually employed.

Since the gypsum which is formed as one of the products of the reaction constitutes an excellent filtering medium if precipitated from solutions of the proper concentration and temperature the filter bed has certain advantages over the filter press.

Another very important difference between more modern practise and that described by Fritsch is that today the sulfuric acid employed in decomposing the phosphate rock or bone has a concentration of 28° to 30° Bé. and hence the phosphoric acid obtained is correspondingly stronger.

Finally the acid liquor is seldom concentrated by direct heat as described by Fritsch. Such a method entails considerable risk of decomposing the ortho acid.

This general plan of producing phosphoric acid, however, is still employed by some of the smaller manufacturers of phosphoric acid

⁴ While the method of concentrating phosphoric acid with steam heated lead coils may have been discontinued in Europe it is still successfully practised in this country.

and double superphosphate, but the large operator has adopted the more modern system of continuous counter current decantation.

The Continuous Counter Current Decantation System.

The application of the continuous counter current principle to the treatment of phosphate rock has simplified considerably the sulfuric acid process of producing phosphoric acid, and though the initial cost of such an installation is relatively heavy, the advantages gained in reduced labor costs, high recoveries of a fairly concentrated product and the decrease in the quantity of fuel and power required have made this method both practical and economical.

The counter current system of removing soluble salts from insoluble material is based on sound economic principles and has been employed in a great many industrial processes, but probably the most highly developed and widely used system of continuous counter current decantation is that known as the Dorr process.

This process as applied to the production of phosphoric acid from phosphate rock is carried out as follows:

The phosphate rock is first ground so that 90 per cent will pass an 80 mesh screen. This rock, together with the proper proportion of sulfuric acid is run into a series of three or four lead lined mixing vats (fitted with stirring devices) wherein the materials receive a preliminary mixing and the chemical reactions begin. Ordinary chamber acid is employed, but this is diluted to 27° to 30° B \acute{e} . with 16° B \acute{e} . phosphoric acid obtained from the second of a series of Dorr thickeners described below. The heat generated by the dilution of the sulfuric acid together with that evolved by the reactions between the acid and the rock raises the temperature of the solutions almost to the boiling point.

After the preliminary mixing the contents of these vats are discharged into the first of a series of three agitator tanks.

The Dorr agitator tank for phosphoric acid production consists of a flat bottom tank with an acid proof lining. The stirring and agitating device consists of a central vertical cylinder carried by a shaft supported from the top of the tank and equipped with two hinged arms carrying plows. These plows travel around the bottom of the tank, moving the solid materials towards the center where they are raised through the hollow shaft or cylinder by means of compressed air and distributed uniformly over the surface of the tank's contents by means of suitable revolving launders. This machine can be operated continuously since the arms sweep the bottom of the tank and the compressed air device constantly stirs up and raises the solids to the surface, preventing accumulations of unacted-on materials.

In the agitator tanks the decomposition of the phosphate is completed—the material from the first tank discharging continuously into the second tank, and the second tank into the third. The time required for this decomposition ranges from four to six hours, depending on the type of rock employed and the rapidity of the reaction.

From the third or last agitator tank the acid solution and suspended solids are pumped to the center of the first of a series of Dorr thickeners. This apparatus consists of a comparatively shallow flat bottom tank (lined with acid resisting material) provided with a slow moving mechanism made up of a central vertical shaft driven by a worm gear and worm and having four arms attached to its lower end. The machine is so arranged that the shaft and arms can be raised and lowered at will. These arms carry plows set at an angle to move the settled or "thickened" material slowly to a discharge opening in the center of the pan's bottom where it is pumped to the second thickener. Both the acid liquor and thickened material discharge into a trough which leads to a distributing box or launder at the center of the pan. A peripheral launder collects the relatively clear phosphoric acid (27° to 30° B \acute{e} .) which overflows the top of the tank, and this launder in turn discharges into a conduit through which the acid is pumped to the evaporators to be concentrated. Where the acid is to be used for the preparation of pure chemicals or for food purposes it must be filtered and put through a purification process such as is described in a subsequent chapter.

The saturated residue or pulp discharged from the base of the first thickener is pumped to the second, and the overflow from this second thickener which has a concentration of from 15° to 16° B \acute{e} . is pumped to the premixers where it is used for diluting the sulfuric acid employed in decomposing the phosphate rock as previously described.

The insoluble residue with its absorbed solution of dilute phosphoric acid is discharged from the second thickener into a third and from this into a fourth, fifth and sixth thickener before it is finally discarded washed practically free of soluble P_2O_5 . The clear liquid which overflows the sides of each thickener into a peripheral launder is conducted through a trough and discharges into a distributing box in the center of the thickener immediately ahead of it, and thus serves to extract the soluble matter out of the sludge received from the preceding thickener which is discharged into the same distributing box. In this way the residues flowing in one direction are constantly being depleted of soluble materials (chiefly P_2O_5) while the series of solutions flowing in the opposite direction (counter current) are continually growing more concentrated.

A flow sheet showing this continuous counter current system as

obtained directly and hence the time, equipment and expense incident to evaporating relatively weak solutions are avoided.

The Purification of Phosphoric Acid.

No matter how pure may be the raw materials employed in its manufacture, the bulk of the phosphoric acid which is to be used for food and chemical purposes must be purified.⁵

The procedure and number of steps required in the purification of phosphoric acid depend on the method employed in manufacturing the acid and the type of the raw material.

In the volatilization process for instance, the bulk of the non-volatile impurities present in the phosphate rock are left in the residue or slag and with due precautions only very small quantities of silica, lime and iron and aluminum phosphates are carried over and are condensed or dissolved in the acid collected. Volatile impurities, however, such as sulfur and its compounds, arsenic and fluorine compounds may be present in such acid and since lead is often employed in some part of the collecting or storage equipment the acid must as a rule be treated to remove this impurity.

Where phosphoric acid is produced from phosphate rock by the sulfuric acid process, its purification and concentration entail considerable time and manipulation. Such acid always contains a number of impurities which are objectionable for one or more of the following reasons:

- (1) They reduce the acidity of the product.
- (2) They render the products manufactured therefrom more difficult to handle.
- (3) They yield products of poor color and of inferior grade.
- (4) They cause certain products (baking powders) to have poor keeping qualities.
- (5) They may render food products unwholesome or actually deleterious to health.

Silica and Calcium Sulfate.

These are solid impurities obtained almost coincident with the treatment of phosphate rock with sulfuric acid—silica being present in the rock and calcium sulfate being formed in the reaction.

They may either be removed in part by counter current decantation as in the Dorr system, or taken out in a filter press. In either event

⁵ There is, however, a relatively small tonnage of syrupy phosphoric acid produced directly by burning elemental phosphorus and this may be sufficiently pure to require no further treatment.

washing with water or dilute acid is necessary in order to reduce to a minimum the loss of phosphoric acid absorbed or entrained in the residue.

It is almost impossible to remove all of the phosphoric acid from the calcium sulfate precipitate and Meckstroth⁶ states that there is usually from 1 to 2 per cent of soluble and from 1 to 2½ per cent of insoluble P_2O_5 left in this residue. This estimated loss, however, appears rather low to the writers, since in average practice the quantity of P_2O_5 undissolved from the rock and entrained in the calcium sulfate precipitate is more nearly 10 per cent of that originally present in the mineral.

Owing to the solubility of calcium sulfate in relatively dilute phosphoric acid, an appreciable quantity (from 1 to 3 per cent) of this compound is held in solution. This, however, is removed by subsequent treatment.

Very little of either of these impurities (silica and calcium sulfate) are contained in the phosphoric acid produced by the volatilization process provided proper precautions are taken in treating the gases of combustion before precipitating or condensing the acid contained therein.

Arsenic.

It is needless to say that it is of the utmost importance to remove all but the smallest traces of this poisonous element from phosphoric acid which is to be used for food and chemical purposes.⁷

Since much of the sulfuric acid (produced from pyrites by the chamber method) and sometimes phosphate rock, contain appreciable quantities of arsenic, the phosphoric acid produced by the sulfuric acid process must be treated to remove this very objectionable impurity. Fortunately arsenic is readily precipitated either by passing a stream of hydrogen sulfide gas directly into the acid or adding a soluble sulfide which is acted on by the acid to form hydrogen sulfide.

After the arsenic is precipitated, the excess of hydrogen sulfide must be removed from the acid since the presence of this gas even in small quantities interferes with subsequent filtration—colloidal sulfur or compounds being formed which clog the filtering media. Meckstroth⁸ states that by heating the acid and sulfide to not less than 40°

⁶ *Manufacture of Phosphoric Acid and Phosphates*, Chem. & Met. Eng., Vol. 26, No. 2, p. 77 (1922).

⁷ The upper limit for arsenic in baking powder set by the National Pure Food and Drug Act is 2 parts per million.

⁸ *Manufacture of Phosphoric Acid and Phosphate*, Chem. & Met. Eng., Vol. 26, No. 2, p. 77 (1922).

to 60° C. no trouble should be experienced in getting rid of the arsenic. But the elimination of the hydrogen sulfide is practically assured in the next treatment.

Iron, Aluminum and Fluorine.

These impurities are the most costly to remove from phosphoric acid since when precipitated they carry with them very appreciable quantities of phosphoric acid which is so combined that it cannot be recovered by leaching the precipitate with water or dilute acid.

The removal of these three impurities is brought about by the addition of finely ground limestone to the acid. During the violent reaction which ensues the solution heats up and the large volume of CO_2 evolved carries off any residual H_2S which may still be in the acid.

This treatment with limestone produces a solution of monocalcium phosphate, a certain amount of dicalcium phosphate and precipitates iron and aluminum phosphates, calcium fluoride and fluosilicates.

The free acidity of the resulting solution is reduced by this treatment to about 4.5 per cent.

This mixture of insoluble compounds is then removed from the acid solution of monocalcium phosphate either by passing through a wooden frame filter press, or a rotary filter of the Oliver type, or it may be separated by counter current decantation. The residue has a high absorptive capacity for soluble salts and hence it is necessary to wash it thoroughly in order to reduce to a minimum the losses of soluble P_2O_5 . The soluble phosphate in the wash water is often precipitated as dicalcium phosphate by the addition of lime and this dicalcium phosphate in turn is filtered off, added to the monocalcium phosphate solution and reconverted into phosphoric acid as described below.

The monocalcium phosphate solution after the removal of the iron, aluminum and the bulk of the fluorine, is then mixed with pure sulfuric acid and insoluble calcium sulfate thus precipitated and filtered off. The phosphoric acid thus obtained is nearly free from all objectionable impurities but since it seldom has a strength of over 30° Bé. (40 per cent $\text{H}_3\text{P}(\text{O}_4)$) it must be concentrated to 50° Bé. before it is suitable for the market. This concentration is accomplished either by passing the weak acid over steam heated lead coils, through acid-proof brick concentrators, or by means of hot air passed counter current to the acid, introduced into a chamber in the form of fine spray. During the concentration process, any residual fluorine compounds still present in the acid are driven off as hydrofluoric acid and crystals of calcium sulfate settle out. The acid is apt to assume a dark color due to the carbonization of the organic matter contained therein, so it is often necessary

to add some oxidizing agent such as a chlorate or permanganate to oxidize this organic matter and obtain a clear water white acid.

In order to throw out any calcium sulfate still in solution and to facilitate the removal of the last traces of lead, a small quantity of either dicalcium phosphate or calcium carbonate is added to the concentrated acid just before the final filtration. The acid is then ready for the market or for use in the manufacture of pure monocalcium or monosodium phosphate.

Vanadium.

Some of the phosphate rock occurring in the Western States, Utah, Idaho, Wyoming and Montana, contain appreciable quantities of vanadium. Phosphoric acid manufactured from such rock by the sulfuric acid process has a green color which renders it unfit for the manufacture of food products unless this vanadium is removed. Laist⁹ has patented a process for the removal and recovery of this impurity which consists in treating the acid with a sufficient quantity of sodium ferrocyanide to precipitate all of the vanadium and most of the iron. The precipitate is filtered off, digested with caustic soda and the sodium ferrocyanide thus regenerated and used over again.

Where the volatilization process is employed in producing phosphoric acid the subsequent removal of iron and aluminum and vanadium should not be necessary so that the most costly and tedious steps in the purification process are eliminated.

The lead and arsenic, however, are removed from such acid in the manner just described, but the fluorine is taken out by the addition of either sodium silicate¹⁰ or sodium phosphate, both of which precipitate insoluble sodium fluoride or sodium fluosilicate. Since such acid is usually collected in concentrated form no subsequent evaporation is necessary so that the only other step required in preparing it for the market is that of filtration. This is usually done on filter beds made up of sand and gravel with perhaps a little charcoal added to remove any coloring matter.

In the preparation of phosphoric acid from high grade bone it is also unnecessary to treat the solution for the removal of iron and aluminum. Otherwise, however, the purification and concentration of the acid must be conducted in a manner similar to that employed in the preparation of phosphoric acid from phosphate rock.

Owing to the high cost and limited supplies of bone and bone products a relatively small percentage of the phosphoric acid produced today is derived from this source.

⁹ U. S. Patent 1,544,911 (1925).

¹⁰ Carothers and Gerber, U. S. Patent No. 1,487,205 (1924).

Crystallized Phosphoric Acid.

Theoretically the ideal way to obtain phosphoric acid absolutely free from all impurities is to crystallize this compound, but while this has been done in a relatively small way the method has not as yet been applied on a commercial scale.

In U. S. Patent No. 1,451,786 (1923), Ross, Durgin and Jones describe a process for purifying phosphoric acid which may be briefly outlined as follows:

Phosphoric acid (produced by the volatilization process) is brought to a specific gravity of 1.85 either by dilution with water or by evaporation; care being taken that the acid solution is not heated above 150°C . The acid is then cooled to 20°C . and inoculated with a crystal of $\text{H}_3\text{P}(\text{O})_4$, whereupon the whole mass solidifies. The crystalline mass is then centrifuged and the crystals thus separated from the mother liquor and dried. The dried crystals are nearly free from impurities, but if it is desired to purify them still further, a little water may be added and the process repeated.

The mother liquor may be used over again in the cycle or employed directly for the manufacture of products where highly purified acid is not so essential.

A modification of this method of purification described by Carothers and Gerber¹¹ is said to be particularly applicable to acid produced by the volatilization process. The process consists in first treating acid having a concentration of over 82 per cent of $\text{H}_3\text{P}(\text{O})_4$ with sodium sulfide and silicate of soda to remove the arsenic and fluorine compounds. The suspended matter is then allowed to settle and the acid filtered, aerated at 50°C . to remove volatile matter, cooled to 10°C . and inoculated with a crystal of phosphoric acid. The mass of crystals formed under these conditions is then separated from the mother liquor by centrifuging.

In a recent article by Ross, Jones and Durgin¹² these investigators show that phosphoric acid produced by the volatilization process when crystallized has a purity superior to that which has been put through elaborate chemical treatments. They have also worked out a chart showing the solubility of both anhydrous and hydrated crystalline phosphoric acid which should be of considerable value as a means of determining the yield of the two types of crystals under the varying conditions of concentration and temperatures. This chart (Figure 39) and their description of its use are given below.

"The solubility curve AB of anhydrous phosphoric acid and that

¹¹ U. S. Patent No. 1,538,089 (1925).

¹² Purification of Phosphoric Acid by Crystallization, Ind. & Eng. Chem., 17, 1021 (1925).

portion CDE of the curve of the hydrated acid above 15° C. are represented in the figure. By use of these curves the amount of acid that will be deposited on crystallizing from a solution of known concentration and temperature may be readily estimated. Thus at 24° C. for example, no crystallization will occur below a concentration of 86.3 per cent. Above this concentration a hydrated crystal will induce partial

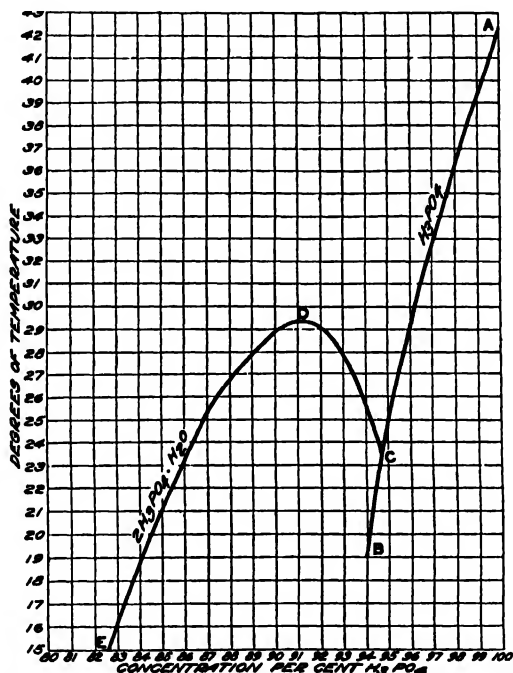


FIG. 39—Solubility Curves of Hydrated and Anhydrous Orthophosphoric Acid

crystallization in the solution, the proportion increasing up to 91.6 per cent when the whole mass becomes solid. With still greater concentrations partial crystallization again occurs until at a concentration of 94.6 per cent no crystallization follows inoculation with either hydrated or anhydrous crystals. This holds true up to 94.8 per cent acid. Above this concentration partial crystallization will follow inoculation with an anhydrous crystal the amount deposited increasing up to 100 per cent when it crystallizes to a solid mass. The curves also show that at 24° C. no crystallization will take place when a 94.8 per cent solution is inoculated with either a hydrated or anhydrous crystal or both, but

that the whole mass becomes solid when the temperature of the solution is lowered one degree or more."

Unfortunately for this method of purifying phosphoric acid, the temperature to which the acid is subjected before crystallization has a marked effect on the rate at which crystallization takes place, and according to the authors just cited, acid which has been maintained at a temperature of 130° C. or above for a protracted period will not crystallize. Any acid produced by the sulfuric acid process which is to be purified by this method therefore must be concentrated at a temperature not exceeding 100° C., which practically precludes the use of anything but steam evaporators operating under reduced pressure.

Chapter 7.

The Volatilization Process for Producing Phosphoric Acid.

Introduction.

In recent years pyrolytic methods of producing phosphoric acid have been receiving a great deal of consideration, and rather exhausting investigations have been conducted in the Bureau of Soils, U. S. Dept. of Agriculture, with a view to establishing their commercial possibilities. From the data obtained and the progress so far made on this problem both by the government agency and by outside commercial interests, there is little doubt that this process will be widely employed to supplement the now almost universally applied method of making water-soluble phosphates by treating phosphate rock with sulfuric acid.

While the volatilization process for producing phosphoric acid has only recently assumed much prominence, the general scheme employed is by no means a new one, it being based on the old method so long in use for the manufacture of elementary phosphorus.

The fundamental principle involved is that at high temperatures (1600° to 1800° C.) silica assumes the properties of a relatively strong acid in so far as its ability to combine with bases is concerned, and therefore it can displace the phosphoric acid of phosphate rock forming silicates of lime and free phosphoric anhydride (P_2O_5). The latter compound being highly volatile at elevated temperatures is driven off as a fume and may be collected either by absorption in water or by means of the Cottrell electrical precipitator. When carbon or coke is added to the mixture to be smelted elemental phosphorus is produced, and if reducing conditions are maintained throughout the operation the decomposition of the rock and expulsion of its phosphorus content may be brought about at considerably lower temperatures (1,300° to 1,500° C.).

According to Nielsen,¹ while tricalcium phosphate and silica begin to react at a temperature of 1,150° C. and continue to form various

¹ Ferrum, Vol. 10, pp. 97-111 (1913).

compounds up to 1650°C ., unless a reducing agent is present these chemical changes merely consist in certain combinations of the two substances and no phosphoric acid is evolved. This same author states that while CO will not reduce tricalcium phosphate this latter compound is completely reducible by carbon, the reduction beginning at 1400°C . He claims, however, that there always remains some phosphorus in the residue because the CaO formed unites with the undecomposed calcium phosphate to form more basic compounds of phosphoric acid which are not reduced by carbon. Peacock² takes issue with Nielsen on this point, stating that if the evolved gases are removed as fast as they are formed complete dispersion of phosphorus is obtained by heating mixtures of phosphate rock and carbon, and Ross Mehring and Jones³ state that if pure tricalcium phosphate mixed with one fifth of its weight of carbon be heated to 1400°C . in a reducing atmosphere, 96 per cent of the phosphorus contained therein is volatilized, and if the temperature be carried to 1550°C ., the dispersion of phosphorus is complete. Nielsen is wrong, however, in his conclusion that P_2O_5 is not evolved upon heating mixtures of phosphate rock and silica in the absence of a reducing agent, for later experimentation has shown that where a relatively high percentage of silica is added phosphoric acid is driven off when the temperature of the mass approaches 1800°C .

The presence of a reducing agent is essential, however, in order to bring about the volatilization of phosphoric acid (or phosphorus) at the lower temperatures. Some early investigators as well as the writer observed that by heating finely ground mixtures of phosphate rock, silica, and coke under reducing conditions the volatilization of phosphorus begins considerably below $1,300^{\circ}\text{C}$., and by prolonged heating at this temperature the bulk of this element may be driven off.

This fact has been confirmed by the experiments of Ross, Mehring and Jones who heated mixtures of phosphate and silica with different proportions of carbon in a strictly reducing atmosphere and were able to obtain as high as 96.7 per cent elimination of phosphorus at a temperature of 1300°C . These investigators have calculated the decomposition temperatures of calcium phosphate mixed with silica and carbon singly or combined and have found that these calculated temperatures checked fairly closely with those observed in actual experiments.

The following table (Table XXXIV) is taken from the article just quoted:

² Amer. Fertilizer, Vol. 39, p. 67 (1913).

³ Ind. & Eng. Chem., Vol. 16, No. 6, p. 563 (1924).

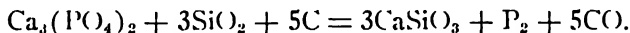
TABLE XXXIV

DECOMPOSITION TEMPERATURES OF CALCIUM PHOSPHATE IN REACTION WITH SILICA AND CARBON, SINGLY OR COMBINED, UNDER A PRESSURE OF ONE ATMOSPHERE

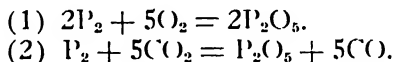
Reaction	Calories	Temperature
$\text{Ca}_3(\text{PO}_4)_2 + 5\text{C} = 3\text{CaO} + \text{P}_2 + 5\text{CO}$	418,900	1,385
$\text{Ca}_3(\text{PO}_4)_2 + 8\text{C} = \text{Ca}_3\text{P}_2 + 8\text{CO}$	* 664,920	1,690
$\text{Ca}_3(\text{PO}_4)_2 + 8\text{C} = 3\text{Ca} + \text{P}_2 + 8\text{CO}$	749,920	1,680
$\text{Ca}_3(\text{PO}_4)_2 + 3\text{SiO}_2 = 3\text{CaO} \cdot \text{SiO}_2 + \text{P}_2\text{O}_5$	105,850	2,310
$\text{Ca}_3(\text{PO}_4)_2 + 2\text{SiO}_2 = (\text{CaO})_2(\text{SiO}_2)_2 + \text{P}_2\text{O}_5$	* 109,400	2,390
$2\text{Ca}_3(\text{PO}_4)_2 + 3\text{SiO}_2 = 3(\text{CaO})_2 \cdot \text{SiO}_2 + 2\text{P}_2\text{O}_5$	233,900	2,550
$\text{Ca}_3(\text{PO}_4)_2 + \text{SiO}_2 = (\text{CaO})_2 \cdot \text{SiO}_2 + \text{P}_2\text{O}_5$	130,850	2,860
$\text{Ca}_3(\text{PO}_4)_2 + 3\text{SiO}_2 + 5\text{C} = 3\text{CaO} \cdot \text{SiO}_2 + \text{P}_2 + 5\text{CO}$	365,350	1,190
$\text{Ca}_3(\text{PO}_4)_2 + 2\text{SiO}_2 + 5\text{C} = (\text{CaO})_2(\text{SiO}_2)_2 + \text{P}_2 + 5\text{CO}$..	* 368,900	1,200
$2\text{Ca}_3(\text{PO}_4)_2 + 3\text{SiO}_2 + 10\text{C} = 3(\text{CaO})_2 \cdot \text{SiO}_2 + 2\text{P}_2 + 10\text{CO}$	752,900	1,260
$\text{Ca}_2(\text{PO}_4)_2 + \text{SiO}_2 + 5\text{C} = (\text{CaO})_2 \cdot \text{SiO}_2 + \text{P}_2 + 5\text{CO}$	390,350	1,280

* Estimated.

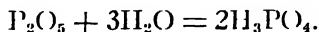
While various silicates of lime are no doubt formed in smelting mixtures of phosphate rock, sand, and coke, depending on the silica-lime ratio in the charge, the general course of the reaction is usually represented by the following simple equation:



The phosphorus evolved is oxidized by air or carbon dioxide to phosphorus pentoxide according to the following equations:



Actual experience has proven, however, that in oxidizing phosphorus either with air or carbon dioxide in the presence of moisture the final product is orthophosphoric acid. This reaction is represented thus:



Advantages of the Volatilization Process.

The pyrolytic process of producing phosphoric acid for fertilizer or chemical purposes appears to offer four distinct advantages over the sulfuric acid process even where the actual cost of the power or fuel required per unit of soluble P_2O_5 is somewhat greater than the cost of the sulfuric acid necessary to effect the same result.

(1) This process makes it possible to utilize low or medium grade phosphate deposits which are unfit for treatment with sulfuric acid, either because of their low content of P_2O_5 or their relatively high con-

tent of such impurities as oxides of iron and aluminum. Where the presence of 6 to 8 per cent of these impurities will cause a rock to be rejected as unsuitable for the manufacture of phosphoric acid for food or chemical purposes by the sulfuric acid process or even for the production of acid phosphate, this amount of alumina tends to aid rather than interfere with the reactions sought in the furnace process. Iron likewise, while very objectionable in the sulfuric acid process, causes no trouble in the furnace method other than its tendency to "fix" some of the phosphoric acid in the form of ferrophosphorus.⁴ The formation of a certain amount of this compound, however, does not necessarily mean a loss, since it finds a ready market in the steel industry. The chief impurity in phosphate rock is usually silica, which is often present in such large amounts as seriously to dilute the acid phosphate made therefrom. Yet such phosphates may require further additions of sand in order to obtain the proper silica-lime ratio for successful treatment by the furnace process. In brief the bulk of the impurities which enter the product (acid phosphate) when using the sulfuric acid process are left behind as a residue in the furnace method of making phosphoric acid.

(2) The furnace method of treating phosphate rock makes it possible to dispense with the elaborate washing and screening processes now so extensively employed in Florida and Tennessee to separate the phosphate rock from the gangue or matrix in which it is embedded. As has been previously pointed out, this mechanical separation involves the loss of a great deal of finely divided phosphate which would be practically all saved if the "run-of-mine" material were treated directly by the furnace scheme.

(3) The adoption of this method will largely eliminate the use of sulfuric acid which under present conditions is hauled to the chemical factory and fertilizer plant as acid and hauled away again as gypsum. The chief function of this sulfuric acid is that of a reagent for converting the phosphate rock into a form which is quickly available to crops. In the manufacture of ordinary acid phosphate it dilutes by 50 per cent every ton of phosphate rock thus treated, forcing the ultimate consumer to pay freight and handling charges on relatively valueless material. While it adds sulfur in the form of gypsum, which is recognized as a soil constituent essential for plant growth, it is sold strictly on the basis of its content of available P_2O_5 . Even where sulfuric acid is used to produce phosphoric acid and this latter product subsequently employed to make double acid phosphate, the separation of the gypsum

⁴Swann, Theodore, Production of Ferrophosphorus in the Electric Furnace; Barr, J. A., Production of Ferrophosphorus at Rockdale, Tenn., Trans. Amer. Institute of Min. & Met. Engrs. (1924).

by filtration and the subsequent evaporation of large quantities of water tend to offset any advantage gained in the manufacture of a concentrated product.

(4) By the use of electric or fuel furnaces located near the phosphate mines it is possible to produce (at the source of the raw material)

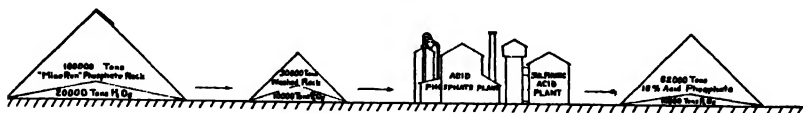


FIG. 40.—Sulfuric Acid Method of Preparing Phosphates. In the present method of preparing soluble phosphatic fertilizers, only one half of the phosphoric acid present in the deposit in the form of washed rock reaches the fertilizer factory. This rock is then treated with an equal weight of sulphuric acid and manufactured into acid phosphate a product containing the same amount of P_2O_5 but in fully twice the bulk.

a relatively concentrated product which will stand heavy handling charges and the cost of long freight hauls. This concentrated product may be either strong phosphoric acid in liquid or crystallized form which can be shipped as such in rubber or lead-lined tank cars or wooden or glass containers and manufactured into food grade phosphates,

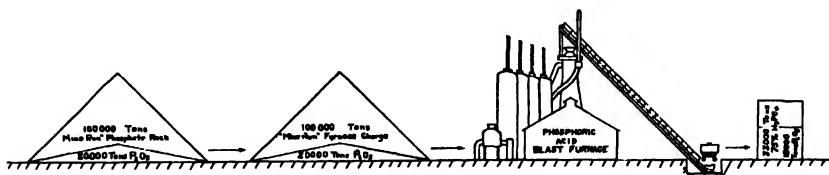


FIG. 41.—Pyrolytic Method of Preparing Phosphate and its Economics. In the furnace process of preparing phosphoric acid, the entire deposit of phosphate may often be utilized, and thus the losses of 50 per cent entailed in washing or purifying the rock eliminated. Assuming a 90 per cent efficiency in the furnace plant, the final product is a liquid containing nearly twice as much P_2O_5 as acid phosphate in a little more than one half the weight.

double acid phosphate (containing from 40 to 50 per cent of soluble P_2O_5) made by treating phosphate rock with this strong phosphoric acid, ammonium phosphate which is produced by passing ammonia gas into phosphoric acid, or a mixture of potassium and ammonium phosphates⁶ which is formed by decomposing a potash salt such as muriate with an excess of phosphoric acid and then neutralizing with ammonia.

⁶ Ross, W. H., Use and Preparation of Concentrated Fertilizers, paper presented at 48th Gen'l Meeting of Amer. Electro Chem. Soc., Sept. 24 (1925).

In any event a product of the highest value occupying but little storage or car space would be obtained which could be readily distributed at the least possible cost.

Figures 40 and 41 show graphically the saving in raw materials (and in the bulk of finished product) which may be effected by treating run-of-mine phosphate by the pyrolytic, or furnace, process instead of putting the material through a washing process and subsequently treating the washed rock with sulfuric acid. In Figures 42, 43, and 44 the

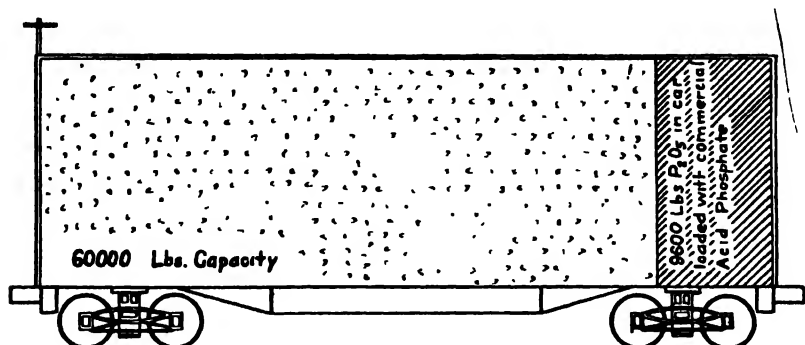


FIG. 42- A car loaded to capacity (60,000 lbs.) with 16 per cent acid phosphate (the standard phosphate fertilizer of to-day) contains only 9600 lbs. of actual phosphoric acid (P_2O_5). Yet transportation and handling charges must also be paid on 84 per cent of gypsum and other impurities contained in this product. Our annual freight bill for transporting acid phosphate is fully \$12,000,000.

economies which may be brought about by shipping these more concentrated products are illustrated.

A Review of Methods for Producing Phosphorus and Phosphoric Acid by Volatilization.

While the production of phosphorus has always depended on the volatilization of this element from its compounds under reducing conditions, in the early days of its manufacture the system employed was elaborate, cumbersome, and costly.^a It involved, first, the treatment of phosphate of lime with sulfuric acid; second, the separation by filtration of the phosphoric acid thus obtained; third, the concentration of this acid by evaporation; and fourth, the mixing of this acid with charcoal or coke and the heating of the mixture to high temperatures

^a Roadman, J. P., *An Account of the Manufacture of Phosphorus*, J. Soc. Chem. Ind., 9, p. 163 (1890).

in clay retorts. Practically every step entailed some loss of the material sought, so the recovery of the phosphorus was very incomplete.

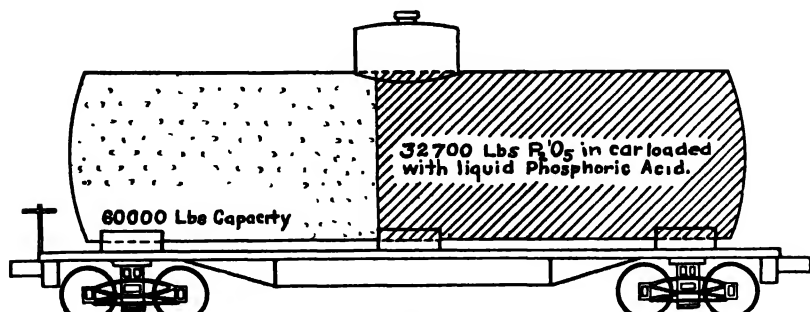


FIG. 43.—A car loaded to capacity (60,000 lbs.) with liquid phosphoric acid (75 per cent H_3PO_4) manufactured by pyrolytic or furnace process contains 32,700 lbs. of actual P_2O_5 or nearly $3\frac{1}{2}$ times as much as that in a car of acid phosphate.

Apparently the substitution of silica for sulfuric acid, so that phosphorus could be produced directly from phosphates of lime, was first

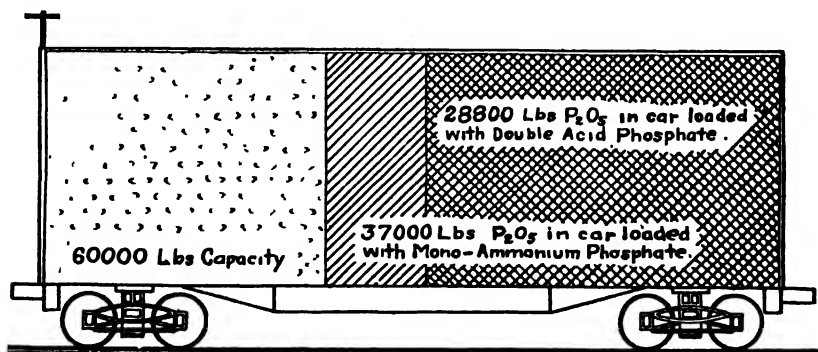


FIG. 44.—A car loaded to capacity (60,000 lbs.) with either double acid phosphate or monoammonium phosphate contains from 28,800 lbs. to 37,000 lbs. of actual P_2O_5 , or from 3 to 4 times as much as that in a car of acid phosphate. By shipping our phosphoric acid (P_2O_5) in these concentrated forms an annual saving of from \$8,000,000 to \$9,000,000 in freight charges alone might be eventually affected on this fertilizer ingredient.

proposed by Auberton and Boblique⁷ in 1867, when these inventors took out a patent for volatilizing and collecting elementary phosphorus from pulverized mixtures of phosphate rock, sand, and coke heated to

⁷ Readman, J. B., J. Soc. Chem. Ind., 9, p. 473 (1890).

a high temperature in closed containers. Two years later (1870) Auberton⁸ advocated the use of a blast furnace for fusing a mixture of phosphates, silica, and coke and driving off and collecting elemental phosphorus; and in 1879 Serve⁹ took out a patent in which he proposed the use of blocks or bricks of an intimate mixture of phosphates and silica bound together by pitch, tar, or coal and smelted in a blast furnace.

The first process for volatilizing phosphoric acid recorded in this country is that of Giles and Shearer,¹⁰ who took out a patent in 1888 for separating this acid from its impurities by passing a current of steam over the acid heated to redness. The distillate consisted of relatively pure phosphoric acid. In 1889 Readman¹¹ proposed to produce elementary phosphorus by heating in an electric furnace (from which air was excluded) a mixture of phosphorus-yielding material (in solution), sand, and coke. Two years later (1891) in an address before the Society of Chemical Industry¹² this inventor stated that he had found it was unnecessary to dissolve the phosphate mineral with sulfuric acid before furnacing, since a mixture of sand and coke decomposes it completely at the temperatures attained in the electric furnace. This general scheme is the one almost universally employed in the manufacture of phosphorus for matches and combustible products. In a general way the processes of Wing,¹³ Duncan,¹⁴ G. C. Landis,¹⁵ and Haff¹⁶ are similar to that proposed by Readman, since (with the exception of that of Wing¹⁷) they all deal with the production of phosphorus by smelting mixtures of phosphate rock, sand, and coke in an electric furnace. Wing and Landis, however, claim advantages for briquetted or molded charges on the basis that the temperature is more easily controlled, dust avoided, and a purer product recovered.

Ruymlbeke¹⁸ appears to have been the first in this country to patent a furnace process for the recovery of phosphoric acid rather than phosphorus. He advocates the use of a blast furnace for treating mixtures of phosphate rock, a reducing agent, and an acid flux, introducing into the upper part of the furnace sufficient air to oxidize any elemental

⁸ Readman, J. B., *J. Soc. Chem. Ind.*, 9, p. 473 (1890).

⁹ *Idem.*

¹⁰ U. S. Patent No. 393,428 (1888).

¹¹ U. S. Patent No. 417,943 (1889).

¹² *J. Soc. Chem. Ind.*, 10, p. 445 (1891).

¹³ U. S. Patent No. 452,821 (1891).

¹⁴ U. S. Patent No. 733,316 (1903).

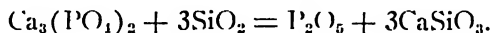
¹⁵ U. S. Patent No. 859,086 (1907).

¹⁶ U. S. Patent No. 1,084,856 (1914).

¹⁷ This inventor proposes the use of a cupola furnace.

¹⁸ U. S. Patent No. 540,124 (1895).

phosphorus. In the processes of De Chalmont,¹⁹ Maywald,²⁰ Levi,²¹ Haff,²² and Wilson and Haff²³ mixtures of phosphate rock and silica are heated in an electric furnace, but no reducing agent is added. The following reaction is assumed to take place:

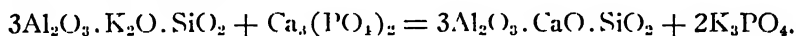


It is proposed to absorb the volatilized P_2O_5 in water to form H_3PO_4 , and Levi²⁴ also suggests adding a salt of soda or potash to the residual slag in the furnace to make a soluble silicate.

The experience of the writers, however, as well as that of a number of other investigators, has been that in the absence of a reducing agent very much higher temperatures must be employed to break the bond between the lime and phosphoric acid in the phosphate rock, and therefore it is poor economic practice to produce phosphoric acid without the addition of carbon or coke when such material can be obtained so cheaply.

Machalske²⁵ suggests that coke and an alkali metal chloride (sodium chloride) be mixed with the phosphate rock in the electric furnace, claiming that phosphorus chloride or hydrochloric and phosphoric acids are volatilized and sodium carbide is produced. He further claims that by introducing nitrogen, sodium cyanide or cyanamid is obtained.

Haff²⁶ and Wilson and Haff²⁷ propose to heat feldspar and phosphate rock in an electric furnace to 2,000° C. without the addition of a reducing agent, claiming that phosphoric acid and potash are simultaneously evolved with the production of potassium phosphate according to the following equation:



These processes are open to the same objection as those of Maywald, Levi, and certain other processes proposed by Wilson and Haff in which no reducing agent is employed, and consequently very high temperatures are required.

Hechenbleikner²⁸ employs carbon or coke in addition to feldspar in smelting the phosphate charge, and the economic possibility of employing silica in the form of greensand, potash shales, feldspar, or

¹⁹ U. S. Patent No. 689,286 (1901).

²⁰ U. S. Patent No. 902,157 (1908).

²¹ U. S. Patent No. 984,769 (1911).

²² U. S. Patent No. 1,076,497 (1913).

²³ U. S. Patent No. 1,076,499 (1913).

²⁴ Loc. cit.

²⁵ U. S. Patents Nos. 789,438, 789,439, 789,440 (1905).

²⁶ U. S. Patent No. 1,018,186 (1912).

²⁷ U. S. Patent No. 1,103,910 (1914).

²⁸ U. S. Patent No. 1,299,337 (1919).

other potash-bearing silicates in the furnace process has been investigated by Ross, Mehling and Jones.²⁹ These investigators showed that both potash and phosphorus can be driven off even at relatively low temperatures provided strict reducing conditions are maintained in the reacting mass.

With a view to producing compounds containing both phosphorus and nitrogen, Peacock³⁰ heated mixtures of phosphate rock and carbon in an atmosphere of nitrogen, claiming that phosphorus and carbonitrides are produced which can be converted into ammonia and ammonium phosphate by treatment with steam. No particular type of furnace is specified by this inventor. As far as known, however, there has been no commercial application of this process.

With a view to the simultaneous production of ferrophosphorus and phosphoric acid or other phosphorus compounds, J. J. Gray³¹ proposes to smelt a mixture of phosphate rock, silica coke, and iron ore in an ordinary blast furnace. The ingredients in the charge are so proportioned that while the maximum displacement of phosphorus from the phosphate rock is sought the amount of iron added in the form of ore is insufficient to take up all of the phosphorus thus evolved. Two blast furnaces for the production of ferrophosphorus are in operation in Tennessee, but in neither case is any elemental phosphorus or phosphoric acid recovered.

Washburn³² and Hechenbleikner³³ have each taken out a great number of patents dealing with processes for the volatilization of phosphoric acid and with types of furnaces in which the reactions may be brought about. Space forbids detailed discussions of all these methods and apparatus, but several which appear to have particularly interesting features are given below.

In Patent No. 1,100,639 (1914) Washburn proposes to charge a mixture of phosphate rock, silica, and carbonaceous material into the shaft of a blast furnace, where the combustion of the fuel is effected and the mass brought to a state of fusion. The molten material is then run into the crucible of an electric furnace, where the final smelting of the charge and complete volatilization of the phosphoric acid is accomplished. In Patent No. 1,314,229 (1919) he describes an apparatus in which are combined certain features of both the blast and electric furnace, and suggests a briquetted mixture of phosphate rock and silica

²⁹ Ind. & Eng. Chem., Vol. 16, No. 6, p. 563, June, 1924

³⁰ U. S. Patents Nos. 1,129,514, 1,129,722 (1915).

³¹ U. S. Patent No. 1,168,495 (1916).

³² U. S. Patents Nos. 1,000,311 (1911); 1,044,957, 1,047,864 (1912); 1,100,639 (1914); 1,373,471 (1921); 1,149,233 (1915); 1,314,229 (1919); 1,359,211 (1920).

³³ U. S. Patents Nos. 1,112,211 (1914); 1,167,755, 1,173,960, 1,202,837 (1916); 1,237,806 (1917); 1,238,336, 1,239,337 (1919).

in order to insure a free passage of the gaseous products through the charge in the shaft. Air is introduced into the shaft to burn the combustible gases and evolved phosphorus and thus preheat the green charge.

Both Hechenbleikner and Washburn describe furnaces³⁴ in which the charge is fed through a rotary kiln and the preheated or partially smelted mass then run into the crucible of an electric furnace, where coke or some other carbonaceous material is added and the remaining phosphoric acid is driven off. By leading the hot and burning gases through the kiln countercurrent to the phosphate charge, heat economies are effected which cut down the energy required in smelting the material in the electric furnace.

Southgate³⁵ describes a combined fuel and electric blast furnace in which the tuyeres are filled with granular coke and supplied with a suitable electric current. A mixture of air and combustible gas or oil is ignited and serves to carry the current into the furnace. Thus the combined effects of fuel and electric energy are obtained.

The most recent method proposed for effecting economies in the production of phosphoric acid is the Liljenroth process³⁶ which consists in collecting the phosphorus evolved from a mixture of phosphate rock silica and coke in the electric furnace, and subsequently oxidizing this phosphorus with steam in the presence of a catalyst. This reaction is represented thus:



The phosphorus pentoxide is converted into phosphoric acid and the hydrogen which is obtained as a by-product is used to produce synthetic ammonia, which in turn is absorbed by the phosphoric acid and converted into diammonium phosphate.

According to a recent report³⁷ the European rights to this process have been purchased by the "Badische Anilin und Soda Fabrik," which is erecting a large plant on the Elbe River, Germany, to produce ammonium phosphate on a commercial scale for fertilizer purposes.

While the feasibility of this process is said to have been proven with a small plant at Niagara Falls, the experience of the author has been that the complete collection of phosphorus requires an elaborate condensing system, which would add appreciably to the cost of the final product. Moreover, the ease with which most catalysts are poisoned makes it seem doubtful if complete oxidation of the phosphorus vapors

³⁴ U. S. Patents Nos. 1,167,755 (1916); 1,299,336, 1,299,337 (1919); 1,359,211 (1920).

³⁵ U. S. Patent No. 1,443,439 (1923).

³⁶ U. S. Patent 1,605,960 (1926).

³⁷ Chem. and Met. Eng., Vol. 33, p. 378 (1926).

will take place on treating them with steam, unless great precautions are taken to prevent contamination of the catalytic agent. The direct oxidation of phosphorus by air as the vapors issue from the furnace appears to be a much simpler scheme even though no valuable by-product is obtained.

Other patented processes and apparatus dealing with the volatilization of phosphorus and phosphoric acid are listed in Tables LXVI and LXVII of the Appendix.

The Use of the Electric Furnace in the Volatilization of Phosphoric Acid.

The first experimental work conducted in the Bureau of Soils on the production of phosphoric acid by the volatilization process was carried on by Ross, Carothers, and Merz³⁸ in an electric furnace. A fair grade of sand and coke and a medium grade of Florida pebble phosphate were employed, these ingredients being mixed in such proportions as to react according to the first equation given on page 207, except that an excess of 20 per cent of both coke and sand were added over that theoretically required.

A furnace of very simple design was used in these early experiments. It consisted of an iron cylinder, 4 feet in diameter and 4½ feet high, lined with 9 inches of fire brick, and provided with a tap hole near the bottom for the removal of the slag. A three-phase alternating current was used, and this was stepped down from 220 volts by two single-phase 75 kilovolt ampere transformers. Each transformer was provided with a split primary, and by joining in different combinations in series and in parallel the coils in the secondary, voltages varying from 40 to 100 in steps of 20 and also halves of these voltages were obtained. A view of this first furnace is shown in Figure 45.

Practically complete volatilization of phosphoric acid from the mixtures given above was readily obtained, but during the preliminary stages of the work great difficulty was experienced in recovering the acid thus evolved, since its absorption in water can only be completely brought about by rather elaborate systems of sprays, baffles, or diving walls, and even then it is impractical to collect all of the P_2O_5 fumes in the form of strong phosphoric acid. These investigators, therefore, decided to try out the Cottrell method of electrical precipitation³⁹ for

³⁸ J. Ind. and Eng. Chem., Vol. 9, p. 26 (1917).

³⁹ Lodge, Sir Oliver, The Electric Disposition of Dust, Smoke, etc., Jour. Soc. Chem. Ind., 5, p. 57 (1886); Cottrell, F. G., Electrical Precipitation of Suspended Particles, Jour. of Ind. and Eng. Chem., 3, p. 542 (1911); Strong, W. W., Electrical Precipitation of Suspended Matter in Gases, Jour. Franklin Institute, 174, p. 239, Sept., 1912; Cottrell, F. G., Electrical Fume Precipitation, Trans. Amer. Inst. Min. Engrs., 43, p. 512 (1912); Cottrell, F. G., Problems in



FIG. 45.— Simple Crucible Electric Furnace at Arlington, Va.

collecting the volatilized acid, and after a good deal of preliminary experimentation built a small plant which proved conclusively that this process could not only be successfully employed but possessed a num-

Smoke, Fume and Dust Abatement, Smithsonian Institution, Report, 1913, p. 653, Publication No. 1307 (1914); Howard, W. H., Fume Precipitation at Garfield, *Bul. Am. Inst. Min. Engrs.*, **49**, p. 540 (1914); Nesbit, A. F., Theoretical and Experimental Considerations of Electrical Precipitation, *Proc. Am. Inst. Elect. Engrs.*, **34**, p. 507 (1915); Strong, W. W., Theory of Electrical Precipitation, *Proc. Am. Inst. Elect. Engrs.*, **34**, p. 220 (1915); Bradley, Linn, Practical Application of Electrical Precipitation, *Proc. Am. Inst. Elect. Engrs.*, **34**, p. 523 (1915); Schmidt, W. A., Cottrell Processes of Electrical Precipitation, *Trans. Canadian Mining Inst.*, p. 110 (1915); Strong, W. W., Some Theoretical Aspects of Electrical Fume Precipitation, *Trans. Am. Electro. Chem. Soc.*, **31**, p. 415 (1917); Heimrod and Egbert, The Cottrell Processes in the Sulphuric Acid Industry, *Chem. Met. Eng.*, **19**, p. 309 (1918); Gellert, N. H., Electrical Cleaning of Blast Furnace Gas, *Blast Furnace and Steel Plant*, **7**, p. 334 (1919);

ber of advantages over the water-absorption system. This was the first time that the Cottrell precipitator was ever used for collecting a product purposely volatilized in order to apply this method of recovery.

Since this same precipitator was used in the early experiments conducted by the senior author and the same general scheme is now employed in commercial installations, a quotation descriptive of the apparatus and its auxiliary equipment taken from the article of Ross, Carothers, and Merz ⁴⁰ is given below.

Cottrell Electrical Precipitator.

"The power used in the precipitator was provided by a 110-volt, 60-cycle, alternating-current motor-generator set, and was stepped up by an 8 kilovolt ampere transformer capable of yielding voltages of 10,000, 20,000, and 40,000 volts. In these experiments the highest voltage only was used. From the transformer the current was changed to intermittent direct current by a small mechanical rectifier attached to the shaft of the generator and so adjusted as to operate in synchronism with it. The positive lead from the direct current side of the rectifier was earthed while the other terminal was connected to the wires suspended in multiple, one in each of the pipes used in the precipitator. Each pipe was then earthed."

"In the preliminary experiments made with this precipitator, sheet-iron pipes were used, 6 inches in diameter and 10 feet high. The precipitated acid, however, had such a corrosive action on these pipes that they had to be abandoned. Pipes were then constructed from ordinary 6-inch glazed terra cotta tile,⁴¹ five sections being taken for each pipe. The precipitated acid gave to the inside of the pipes an effective conductive surface and in grounding the pipes it was found sufficient simply to bring the ground wire to the inside surface of each pipe at one point. Arranged in this way the terra-cotta pipes could be used just as metal pipes and they had the very important advantage of being unaffected by phosphoric acid. Wires of monel metal were found to be least acted upon when suspended in the pipes, but nichrome wire also served quite well.⁴² Weights were suspended at the ends of the wires and individual oscillations were prevented by a wire connecting all the weights.

Landolt and Pier, *Air Cleaning by the Cottrell Electrical Precipitation Processes*, *Bul Am Soc of Heating and Ventil. Engrs.*, January (1920); Hesson, Landolt, and Hemmrod, *Recent Applications of the Cottrell Processes*, *Eng. and Min. Jour.*, 112, p 446 (1921).

⁴⁰ Loc cit

⁴¹ The terra-cotta tile used in commercial installations is usually 8" in diameter.

⁴² Later investigation has shown that sterling silver wire is the most resistant to corrosion under regular working conditions.

"The capacity of the fan used in drawing off the fumes from the furnace was 450 cubic feet per minute. As shown later, this flow of air was much in excess of that necessary to oxidize the phosphorus evolved from the furnace. Using a fan of this capacity it was found necessary to use six pipes to bring about complete precipitation of the fumes.

"Since the phosphorus passes off from the furnace for the most part in the form of phosphorus pentoxide it might be expected at first thought that it would be collected as such in the precipitator. A simple calculation will show, however, that this is not practical, for there will always be enough moisture in the charge used and in the air required to oxidize the phosphorus evolved to convert the phosphorus pentoxide either in whole or in part into phosphoric acid.¹³ . . .

"When the fumes were passed through the tower and precipitation thus made at a temperature but little above normal, the concentration of the acid first collected was in the neighborhood of 60 per cent phosphoric acid. . . . On cutting down the flow of air somewhat the concentration of the acid was increased to about 80 per cent, and it is quite evident that with the humidity of the air remaining the same a still more concentrated acid might be obtained by further limiting the flow of air through the furnace." A view of the furnace used in these experiments is shown in Figure 45.

Larger Scale Experiments.

The results obtained in the preliminary experiments with the electric furnace were so encouraging that it was deemed wise to continue the investigation on a larger scale in order to determine the commercial possibilities of the process. Accordingly a coöperative arrangement was entered into with several firms interested in this line of work and a plant of considerably larger capacity and much better suited for the purpose than that at Arlington Experimental Farm was erected at Hoboken, N. J. Protracted tests were made over a period of several days and weeks, and data obtained from which the cost of producing phosphoric acid by this method was estimated. This work was conducted under the direct supervision of J. N. Carothers, and a quotation from his article ⁴⁴ describing the equipment is given below:

"From the transformer ratings, the plant was a 200-kilowatt installation. The incoming power was quarter phase, 2,400 volts, which was transformed to 3 phase, 220 volts, by a bank of Scott connected

⁴³ In plant practise, however, it has been found necessary to introduce additional water or steam to obtain smoother precipitator action and acid of the proper strength.

⁴⁴ Jour. Ind. and Eng. Chem., 10, No. 1, p. 35 (1918).

transformers. A second bank of transformers and a set of double-throw switches made it possible to have either 220 volts or 110 volts in the furnace. This arrangement was adopted so as to use the higher voltage for starting and the low for operating. For the best operating conditions 110 volts were found satisfactory.

"The furnace consisted of a water-cooled crucible, with the cooled section extending no higher than the region of the molten slag. It was lined with fire-clay brick, but silica brick would prove more satisfactory. The portion not exposed to the action of slag was lined with a fire-clay brick. All gas mains and the cooling tower had a fire-clay brick lining. The heat from the gases served to harden the exposed surface and thus improve the service of the brick. The electrodes entered through the top of the furnace but below a line where the charge entered. Care should be taken in the design of such furnaces that the angle of the electrodes conform with the angle of repose of the charge. Thus as the charge falls in a natural pile, the breakage of electrodes is eliminated. Electrodes may be conveniently controlled by hand, or mechanically. Hand control was used in this experiment, with the control so located that the switchboard and instruments could be observed. Six-inch and four-inch graphite electrodes were used. The life of a 4-inch electrode was about 7 days, while the 6-inch electrodes lasted on an average of 10 days under favorable conditions. Thus it may be seen that with such a low consumption electrodes may be operated by hand, since the chief movement of electrodes is when they are consumed. In this experiment the charge was fed by hand; however, this is obviously impractical in a large installation, where mechanical apparatus should be used. During regular operation about 2,000 pounds of rock were consumed per 12-hour period.

"A slag pit filled with water was used to quench the molten slag as it flowed from the furnace. The slag thus chilled slid to one end and was removed mechanically. The P_2O_5 content of the slag was approximately 2 per cent, although it is possible to reduce it to 1.5 per cent or even one per cent for regular operation. The P_2O_5 content of the slag is largely a matter of the mixing of the charge and using the proper proportions of rock, sand, and coke.

"The average production was 0.3 pound H_3PO_4 per kilowatt hour absorbed; however, there were periodic yields, during times of good operating conditions, in which 0.4 pound H_3PO_4 per kilowatt hour was produced. Judging from the average results of this experiment it seems reasonable to assume that a production of 0.6 pound H_3PO_4 per kilowatt hour is possible. Of course, the production is entirely dependent upon the efficiency of the furnace. In the case of this work no means were adopted to utilize the heat absorbed by the water sur-

rounding the crucible or in the gases carried over from the charge. Also there were heat losses from the oxidation of phosphorus to phosphorus pentoxide (P_2O_5) and carbon monoxide (CO) to carbon dioxide (CO_2) which, if utilized, would materially have increased the efficiency of the process.

"As the gases were removed from the furnace they passed through a cooling tower before entering the treater. This tower was installed to afford sufficient radiation, so that the gases entered the treater at 250 degrees to 300 degrees C. Above these temperatures in the treater electrical and mechanical difficulties arise which make higher temperatures undesirable.

"The treater consisted of a header of common brick, with a reinforced concrete top to support the pipes, and 20 treater tubes of vitrified sewer pipes, 12 inches in diameter and 15 feet in length. All joints were packed loosely with silica to prevent air from entering at these points. The pipes were inclosed to prevent cracking, due to heat differences, and to maintain an even flow of gas.

"All pipes at the top were inclosed in a common hood. Supports for the conductors rested on insulators within the treater hood. Complete clearance was given to 2,000 cubic feet of gas entering at 300° C., with a velocity of 3 linear feet per second. . . . Power was supplied the treater from a 150-volt motor-generator set, and transformed to higher voltages by a 7.5 kilovolt ampere transformer. A 5-point switch on the low-tension side of the transformer, connecting the various turns of coils, made a variation of voltages possible. It was found that 70 kilovolts was sufficient to give complete precipitation of the gases, at the above stated volumes and velocity.

"As the acid fell from the pipes it was caught in a receiving basin of vitrified brick set in acid-proof cement. From this basin the acid flowed out and was disposed of by pumping to a receiving vat. The concentration of the acid collected was controlled by the temperature of the gas in the treater. At a temperature of less than 100° C. the concentration is not likely to exceed 50 per cent H_3PO_4 , while a temperature of 250° to 300° C. will yield an acid of 85 to 93 per cent H_3PO_4 . In one case an acid of 97 per cent was produced. An acid above 85 per cent H_3PO_4 will probably solidify when it reaches atmospheric temperatures, and therefore the pumping apparatus and pipe lines should be so constructed as to prevent clogging."

From the results obtained in this plant Carothers estimated the yield of phosphoric acid (P_2O_5) in a 3,000-kilowatt furnace operating on a 24-hour basis 300 days of the year at 0.22 pound per kilowatt hour. Assuming that power was available at \$25 per horsepower year he estimated the cost of production, exclusive of interest charges,

maintenance, and depreciation, at 3.37 cents per pound of P_2O_5 . While this cost compared rather favorably with that of the P_2O_5 in acid phosphate during the war, when the price of sulfuric acid was exceptionally high, the figures indicated that this process could hardly compete with the older method under normal conditions unless cheaper power or higher efficiency were obtained.

Since these experiments were conducted, electric furnaces of commercial size for the simultaneous production of ferrophosphorus and phosphoric acid have been erected at Anniston, Ala., and the yield of acid per KW hour has been so improved that they are operating quite successfully. While most of the phosphoric acid produced at this plant is purified and sold for the purpose of manufacturing baking powder, and to the pure chemical trade, the president ⁴⁵ of the company states that the experience gained during the last few years "clearly indicates that with cheap hydroelectric power and proper plant location phosphate rock can be smelted in the electric furnace for the production of fertilizer material at a cost comparing very favorably with the present method."

Electric Smelting of Mine-Run Phosphates.

But there is another important factor having a direct bearing on the cost of the unit of P_2O_5 manufactured by the furnace process which was not taken into consideration during these earlier experiments. This is the great saving which can be effected by employing low-grade and run-of-mine phosphates which are either unfit for treatment with sulfuric acid because of the inherent nature of the rock itself, or must be treated by some mechanical means to separate the phosphate from the impurities with which it is associated. With these facts in mind, the senior author undertook a number of experiments with the smaller electric furnace at Arlington Experimental Farm, Va., and while these tests were not conducted over any long period of time, they show that impure phosphates which can be readily and cheaply mined may be advantageously smelted in the electric furnace and the final product not only obtained more cheaply but a great conservation of our phosphate resources effected.

For this work samples of phosphate materials were obtained from each of the following three localities: (1) Mine-run phosphate from the hard-rock regions near Newberry, Fla.; (2) Mine-run phosphate from the pebble fields near Fort Meade, Fla.; (3) Tennessee brown-rock phosphate from old dumps near Mount Pleasant, Tenn. The analyses of these samples of phosphatic material are given in Table XXXV and the volatilization of P_2O_5 obtained from these various

⁴⁵Swann, T., *Ind. & Eng. Chem.*, Vol 14, p. 630 (1922).

types of run-of-mine rock when smelted in the electric furnace are given in Table XXXVI.

TABLE XXXV

ANALYSES OF AIR-DRIED SAMPLES OF MINE-RUN AND WASTE MATERIAL FROM THE FLORIDA AND TENNESSEE PHOSPHATE FIELDS

Constituent	Florida Hard Rock and Matrix	Florida Phosphate (Pebble) and Matrix	Tennessee Brown Phosphate Waste
	Per Cent	Per Cent	Per Cent
CO ₂	2.22	1.53	1.49
SiO ₂	14.37	45.99	14.23
P ₂ O ₅	30.69	15.38	29.85
Al ₂ O ₃ plus Fe ₂ O ₃	5.03	7.50	7.72
CaO	42.07	22.79	40.42
F	3.68	1.58	2.71
Total	98.06	94.77	96.42

TABLE XXXVI

QUANTITY OF PHOSPHORIC ACID (P₂O₅) VOLATILIZED FROM A CHARGE MADE UP OF MINE-RUN PHOSPHATES WHEN SMELTED IN THE ELECTRIC FURNACE FOR 3 HOURS

Phosphatic Material Used in Charge	P ₂ O ₅ in Charge, Exclusive of Coke, CO ₂ and F	P ₂ O ₅ in Slag by Analysis	Proportion of Total P ₂ O ₅ Remaining in Slag After Smelting	Amount of P ₂ O ₅ Volatilized
	Per Cent	Per Cent	Per Cent	Per Cent
Hard-rock phosphate and matrix....	22.0	0.50	1.8	98.2
Land-pebble phosphate and matrix.	19.1	.66	3.0	97.0
Tennessee waste material.....	21.3	.67	2.7	97.3

The figures given in Table XXXVI show a volatilization fully as good as that obtained where high-grade phosphate rock was used, either at Hoboken, N. J., or in the preliminary experiments conducted in this same furnace. No data, however, were collected in this latter experiment that would admit of a comparison between the power consumed

on the mine-run samples and that required for a charge made up of high-grade phosphate rock, sand, and coke, but it seems unlikely that there would be much difference in these figures since the extra power required to smelt the slight increase in the quantity of charge due to the presence of iron and aluminum oxides and perhaps a little extra carbonate of lime, should be more than offset by the lowering of the melting point caused by the presence of these impurities. In the following tables (Tables XXXVII, XXXVIII, XXXIX, XL and XLI) are given the estimated costs of producing the unit of P_2O_5 by the two processes, namely, the sulfuric acid method and the furnace process, from various grades and types of phosphate rock in the form of phosphoric acid, acid phosphate, and double superphosphate.

TABLE XXXVII

ESTIMATED COST (AT THE MINES) OF PRODUCING ONE TON OF AVAILABLE PHOSPHORIC ACID (P_2O_5) BY TREATING HIGH-GRADE WASHED PHOSPHATE ROCK WITH SULFURIC ACID

Item	Florida Hard Rock Phosphate			Florida Pebble Phosphate			Tennessee Brown Rock Phosphate		
	Quantity	Cost per Ton	Total Cost	Quantity	Cost per Ton	Total Cost	Quantity	Cost per Ton	Total Cost
Phosphate rock	Tons 3.18	\$4.00	\$12.72	Tons 3.18	\$3.00	\$9.54	Tons 3.18	\$4.50	\$14.32
Sulfuric acid (50° Bé.)	3.44	* 8.00	27.52	3.44	* 8.00	27.52	3.44	* 8.00	27.52
Labor and repairs	† 1.30	8.61	† 1.30	8.61	† 1.30	8.61
Interest and depreciation	‡ .32	2.12	‡ .32	2.12	‡ .32	2.12
Overhead, taxes, and insurance65	4.3065	4.3065	4.30
Miscellaneous, laboratory, etc.	2.50	2.50	2.50
Total cost per ton of P_2O_5	57.77	54.09	59.37
Total cost per unit of P_2O_5585459

* Cost per ton, including interest, taxes, and insurance.

† Cost per ton of material handled.

‡ 6% interest and 10% depreciation on \$100,000.00 (50,000 tons of acid phosphate).

TABLE XXXVIII

ESTIMATED COST (AT THE MINES) OF PRODUCING ONE TON OF PHOSPHORIC ACID (P_2O_5) BY THE ELECTRIC FURNACE METHOD FROM HIGH-GRADE WASHED PHOSPHATE ROCK

Item	Florida Hard Rock Phosphate			Florida Pebble Phosphate			Tennessee Brown Rock Phosphate		
	Quantity	Cost per Ton	Total Cost	Quantity	Cost per Ton	Total Cost	Quantity	Cost per Ton	Total Cost
	Tons			Tons			Tons		
Phosphate rock	3.32	\$4.00	\$13.28	3.32	\$3.00	\$9.96	3.32	\$4.50	\$14.95
Sand	1.50	.50	.75	1.50	.50	.75	1.50	1.00	1.50
Coke braize75	3.00	2.25	.75	3.00	2.25	.75	3.00	2.25
Power *	24.00	24.00	24.00
Labor and repairs..	10.00	10.00	10.00
Electrodes	2.13	2.13	2.13
Interest and depreciation	2.12	2.12	2.12
Overhead, taxes, and insurance	10.00	10.00	10.00
Miscellaneous, laboratory, etc.	5.00	5.00	5.00
Total cost per ton of P_2O_5	69.53	66.21	71.95
Total cost per unit of P_2O_5706672

* Power at \$25 per horsepower year.

TABLE XXXIX

ESTIMATED COST (AT THE MINES) OF PRODUCING ONE TON OF AVAILABLE PHOSPHORIC ACID (P_2O_5) IN THE FORM OF DOUBLE SUPERPHOSPHATE BY TREATING HIGH-GRADE WASHED PHOSPHATE ROCK WITH PHOSPHORIC ACID OBTAINED BY VOLATILIZATION IN THE ELECTRIC FURNACE

Item	Florida Hard Rock Phosphate			Florida Pebble Phosphate			Tennessee Brown Rock Phosphate		
	Quantity	Cost per Ton	Total Cost	Quantity	Cost per Ton	Total Cost	Quantity	Cost per Ton	Total Cost
	Tons			Tons			Tons		
Phosphate rock	0.98	\$4.00	\$3.92	0.98	\$3.00	\$2.94	0.98	\$4.50	\$4.41
P_2O_5 in form of 58° Bé. acid	* .67	69.53	46.65	* .67	66.21	44.35	* .67	71.95	48.20
Labor and repairs..	† 1.30	2.68	† 1.30	2.68	† 1.30	2.68
Interest and depreciation	‡ .32	.65	‡ .32	.65	‡ .32	.65
Overhead, taxes, and insurance65	1.3065	1.3065	1.30
Miscellaneous, laboratory, drying, etc.	2.50	2.50	2.50
Total cost per ton of P_2O_5	57.70	54.42	59.74
Total cost per unit of P_2O_5585560

* Equivalent to 1.08 tons of H_2PO_4 (58° Bé.).

† Cost per ton of material handled.

‡ 6% interest and 10% depreciation on \$100,000.00 (50,000 tons of double super-phosphate).

TABLE XL

ESTIMATED COST (AT THE MINES) OF PRODUCING ONE TON OF PHOSPHORIC ACID (P_2O_5) BY THE ELECTRIC FURNACE METHOD FROM MINE-RUN PHOSPHATES

Item	Florida Hard Rock and Matrix			Florida Pebble and Matrix			Tennessee Brown Rock Phosphate		
	Quantity	Cost per Ton	Total Cost	Quantity	Cost per Ton	Total Cost	Quantity	Cost per Ton	Total Cost
	Tons			Tons			Tons		
Phosphate and matrix	3.62	\$0.75	\$2 72	4.89	\$0.75	\$3.67	3.73	\$1.00	\$3 73
Washed pebble for reinforcing	1.12	3.00	3.36
Sand	1.64	.50	.82	1.64	1.00	1.64
Coke braize75	3.00	2 25	.75	3.00	2 25	.75	3.00	2 25
Power *	24.00	24.00	24 00
Labor and repairs	10 00	10.00	10 00
Electrodes	2 13	2.13	2.13
Interest and depreciation	2.12	2.12	2.12
Overhead, taxes and insurance	10 00	10.00	10.00
Miscellaneous, laboratory, etc.	5.00	5.00	5.00
Total cost per ton of P_2O_5	59 04	62.53	60.87
Total cost per unit of P_2O_5596361

* Power at \$25 per horsepower year.

TABLE XLI

ESTIMATED COST (AT THE MINES) OF PRODUCING ONE TON OF AVAILABLE PHOSPHORIC ACID (P_2O_5) IN THE FORM OF DOUBLE SUPERPHOSPHATE BY TREATING HIGH-GRADE PHOSPHATE ROCK WITH PHOSPHORIC ACID PRODUCED BY THE ELECTRIC FURNACE FROM RUN-OF-MINE MATERIAL.

Item	Florida Hard Rock Phosphate			Florida Pebble Phosphate			Tennessee Brown Rock Phosphate		
	Quantity	Cost per Ton	Total Cost	Quantity	Cost per Ton	Total Cost	Quantity	Cost per Ton	Total Cost
	Tons			Tons			Tons		
Phosphate rock	0.98	\$4.00	\$3.92	0.98	\$3.00	\$2.94	0.98	\$4.50	\$4 41
P_2O_5 in form of 58° Bé acid	* .67	59.04	39.58	* .67	62 53	41 91	* .67	60 87	40 79
Labor and repairs	† 1.30	2.68	† 1.30	2.68	† 1.30	2 68
Interest and depreciation	‡ .32	.65	‡ .32	.65	‡ .32	.65
Overhead, taxes and insurance65	1.3065	1.3065	1.30
Miscellaneous, laboratory, drying, etc.	2.50	2.50	2.50
Total cost per ton of P_2O_5	50.63	51.98	52.33
Total cost per unit of P_2O_5515252

* Equivalent to 1.08 tons of H_3PO_4 (58° Bé.).

† Cost per ton of material handled.

‡ 6% interest and 10% depreciation on \$100,000.00 (50,000 tons of double super-phosphate).

While the figures given in the foregoing tables are partly estimated, they are considered conservative and fair in so far as the costs of each process and type of material used compares with any other. Summing up the data given in these tables, we find that the cost of the unit of P_2O_5 obtained by the electric furnace process is considerably higher than the present cost of the phosphoric acid produced by the sulfuric acid method, but when the phosphoric acid obtained by the former methods is used to manufacture double acid phosphate, the final cost of the unit of soluble P_2O_5 is brought down very materially.

When run-of-mine phosphate is treated in the electric furnace, however, the cost of the unit of P_2O_5 in the form of acid is considerably below that obtained by the same process using high grade rock, and where the phosphoric acid obtained by smelting such low grade materials is utilized in making double superphosphate, the final cost of the unit of P_2O_5 compares very favorably with that produced by the sulfuric acid method. At this point, however, the double superphosphate has a distinct advantage over the ordinary acid phosphate, in that it is so concentrated that it can be handled, shipped, and distributed at a minimum cost.

Theoretical Heat Balances.

The data obtained in these experiments and given in Tables XXXVIII and XL indicate that where phosphoric acid is produced in the electric furnace the main cost item is that of electric power. Where this electric energy is available at a price as low as \$25 per horsepower year, the actual cost of power is over 70 per cent of the total charge against the ton of P_2O_5 in the form of H_3PO_4 . With a properly designed furnace, however, and efficient auxiliary equipment for conserving the heat wasted in the ordinary crucible type of furnace, it should be possible to reduce the power cost per unit of phosphoric acid very materially. In Tables XLII and XLIII the heat balance of two electric furnaces for the production of phosphoric acid, one an open crucible and the other of the shaft type, are given. Certain assumptions were made in making up these tables, but the figures are considered conservative and comparable in so far as the relative heat economies are concerned. In both instances sufficient carbon is assumed to be present to reduce completely the phosphoric acid to elementary phosphorus and enough silica added to give a slag having the composition $CaSiO_3$.

TABLE XLII

THEORETICAL HEAT BALANCE OF ELECTRIC FURNACE OF SIMPLE CRUCIBLE TYPE
(Capacity 10 tons P_2O_5 per day of 24 hours)

Item No.	Actions Affecting Temperature	Heat Generated (plus)		Heat Consumed (minus)	
		Thousands of Kilo-gram-Calories per Ton ^a of P_2O_5	Per Cent of Total	Thousands of Kilo-gram-Calories per Ton ^a of P_2O_5	Per Cent of Total
1	Absorbed by burden before fusion ^b
2	Absorbed by burden in fusing ^b
3	Absorbed by endothermic reactions in ore	4,100	36.1
4	Evolved by exothermic reactions in ore	420	3.7
5	Evolved by oxidation of C to CO..	1,140	10.0
6	Evolved by oxidation of this CO to CO_2	2,660	23.4
7	Evolved by oxidation of P to P_2O_5	2,850	25.0
8	Removal of heat by cooling masonry	1,619	14.2
9	Removal of heat by slag ^c	1,707	15.0
10	Removal of heat by evolved gases (at 650° C.).....	2,350	20.6
11	Removal of heat by unburned CO ^d	1,600	14.1
12	Heat supplied by electric energy ..	4,306	37.9
	Total	11,376	100.0	11,376	100.0

Economy: ^e

In pounds P_2O_5 per kilowatt hour.....	0.44
In 2,000 pounds P_2O_5 per kilowatt year.....	1.90
In 2,000 pounds P_2O_5 per horsepower year.....	1.43
In over-all thermal efficiency, per cent.....	36.10

^a Metric ton.^b Included in item 9.^c Including small amount removed by ferrophosphorus.^d Assuming one-third of CO unburned in furnace.^e 5,010 kilowatt hours.^f Production based on 90 per cent recovery of P_2O_5 in furnace charge.

TABLE XLIII

THEORETICAL HEAT BALANCE OF ELECTRIC FURNACE, SHAFT TYPE
(Capacity 10 tons P_2O_5 per day of 24 hours)

Item No.	Actions Affecting Temperature	Heat Generated (plus)		Heat Consumed (minus)	
		Thousands of Kilo-gram-Calories per Ton ^a of P_2O_5	Per Cent of Total	Thousands of Kilo-gram-Calories per Ton ^a of P_2O_5	Per Cent of Total
1	Absorbed by burden before fusion ^b
2	Absorbed by burden in fusing ^b				
3	Absorbed by endothermic reactions in ore				
4	Evolved by exothermic reactions in ore	420	4.5	4,100	44.1
5	Evolved by oxidation of C to CO..	1,140	12.3
6	Evolved by oxidation of this CO to CO_2	2,660	28.6
7	Evolved by oxidation of P to P_2O_5	2,850	30.6
8	Removal of heat by cooling masonry	2,369	25.5
9	Removal of heat by slag ^c	1,707	18.3
10	Removal of heat by evolved gases (at 315° C.).....	1,124	12.1
11	Removal of heat by unburned CO ^d
12	Heat supplied by electric energy...	* 2,230	24.0
	Total.....	9,300	100.0	9,300	100.0

Economy: ^f

In pounds of P_2O_5 per kilowatt hour.....	0.85
In 2,000 pounds P_2O_5 per kilowatt year.....	3.70
In 2,000 pounds P_2O_5 per horsepower year.....	2.77
In over-all thermal efficiency, per cent.....	44.10

^a Metric ton.^b Included in item 9.^c Including small amount of ferrophosphorus.^d Assuming all CO burned in furnace crucible and shaft.^e 2,595 kilowatt hours.^f Production based on 90 per cent recovery of P_2O_5 in furnace charge.

It will be noted that under these conditions the over-all furnace reactions are exothermic. If, therefore, no heat were lost in the evolved gases, in unburned carbon monoxide, from radiation through the walls of the furnace, and in the slag which is tapped off, the reaction when started should go to an end without power consumption. Of course some of these losses cannot be avoided and others can only be partially eliminated, but as will be seen by comparing the figures for the two types of furnaces the efficiency of the shaft type, wherein much of the

heat in the effluent gases is conserved and the phosphorus and CO are completely oxidized before leaving the furnace shaft, a great saving in power consumption may be effected.

With the development of certain power sites it is possible that electric energy may be obtained for purposes such as fertilizer production at a price below \$25 per horsepower year. This would make it feasible either to transport and use higher grade phosphate rock from the Florida fields or to transmit such power to the Tennessee phosphate fields and use run-of-mine phosphates, thus eliminating the costly washing process and conserving and utilizing deposits which are at present considered unfit for the production of phosphatic fertilizers.

The work of Ross, Mehring and Jones, which shows that phosphorus can be driven off from mixtures of phosphate rock, silica, and carbon at a temperature below the fusing point of such a charge (1300° C.), is now being conducted on a somewhat larger scale and if the mechanical and chemical difficulties can be successfully met it may be possible to produce phosphorus and phosphoric acid with the expenditure of far less electric current than is required in the electric arc furnace. These semi-commercial experiments are being conducted by K. D. Jacob.⁴⁶

The Use of the Fuel Furnace in the Volatilization of Phosphoric Acid.

At the present time, however, there is very little cheap electric power available in this country. Moreover, the history of our hydroelectric developments in the past has shown that the demand for primary power for public utilities and for industries turning out relatively high-priced products has been so great that the manufacturer of lower-priced goods which depend upon smelting processes has had to look to fuel for his source of energy. Even should there be a great increase in our power developments, many believe that it will still be economically unsound to dispose of this power for the manufacture of a material as cheap as phosphate fertilizer must always be.⁴⁷

Comparative Cost of the Thermal Unit Furnished by Electric Power and Fuel.

In the volatilization process of producing phosphoric acid, however, the chief function of the electric current is that of supplying the

⁴⁶ Development of Volatilization Methods for the Manufacture of Phosphoric Acid, 48th Meeting of the American Electro Chemical Society, Chattanooga, Tenn., Sept. 24, 1925.

⁴⁷ MacDowell, C. H., Problems of Muscle Shoals, a paper prepared for the Muscle Shoals Inquiry (1925). Reprinted in American Fertilizer, Vol. 63, p. 21 (1925).

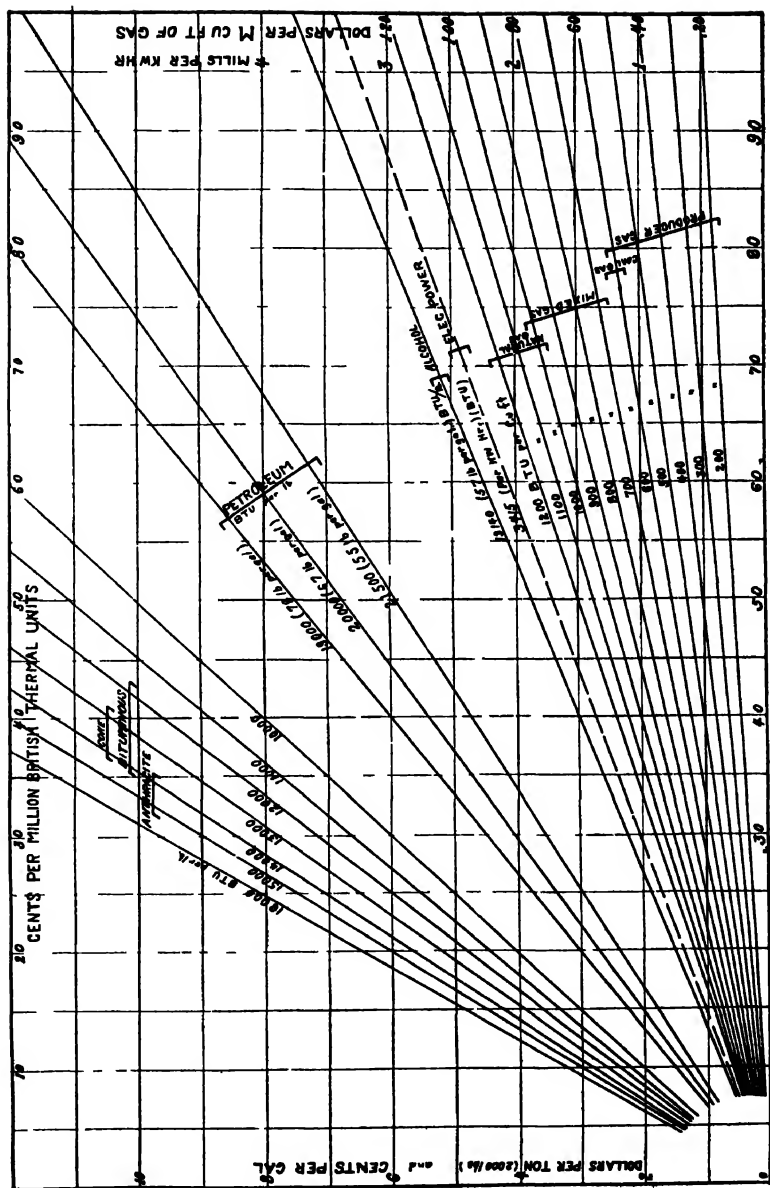


FIG. 46.—Comparative Cost of Million B. T. U. Furnished by Electric Power and Fuel.

temperature necessary to effect the chemical reactions involved and the electric furnace is merely a convenient type of apparatus to use in bringing about the decomposition of phosphate rock under reducing conditions. It logically follows, therefore, that if these same conditions can be fulfilled by employing fuel as a heating source in lieu of the electric arc, a great saving in the cost of the heat energy required should be effected. The accompanying charts (Figures 46-48) and Table XLIV give a fairly clear idea of how electric power and fuel compare in cost as sources of equivalent quantities of heat energy.

TABLE XLIV

PRICES ASSUMED FOR ELECTRIC POWER AND CORRESPONDING COSTS OF STANDARD FUELS AS SOURCES OF EQUIVALENT QUANTITIES OF HEAT

Electric Power ^a Cost per Kilowatt Year	Maximum Prices at Which Standard Fuels Must Be Obtained to Compete with Electric Power at Rates Given in Column I			
	Coal ^b per Long Ton	Fuel ^c Oil per Gallon	Coke ^d per Long Ton	Natural Gas ^e per Thousand Cubic Feet
\$5	\$4 60	\$0 022	\$4 60	\$0 18
10	9 20	044	9 20	36
15	13 80	066	13 80	54
20	18 40	088	18 40	72
25	23 00	110	23 00	90
30	27 60	132	27 60	1 08
35	32 20	154	32 20	1 26
40	36 80	176	36 80	1 44

^a 3,415 Btu per kilowatt hour

^b 14,000 Btu per pound

^c 19,000 Btu per pound

^d 14,000 Btu per pound

^e 1,200 Btu per cubic foot

In the curves given in Figure 46 the cost of a million British thermal units produced by certain standard fuels at various prices is compared with the cost of the heat equivalent produced by electric power at various rates per kilowatt hour.

In Figure 47 curves are given for converting the cost of the thermal unit from mills per kilowatt hour into the terms of dollars per kilowatt year or dollars per horsepower year, either of which is a more conventional method of expressing the cost of power which is consumed in large blocks.

In Table XLIV certain points along the curves given in Figure 46 are taken in order to show typical examples of the prices at which electric power must be obtained to compete with fuel furnishing the same number of thermal units.

In Figure 48 a comparison is made of the yield of product obtained

by burning 1 pound of various fuels with that obtained by a power consumption of 1 kilowatt hour. This last chart is drawn up on the assumption that the same efficiency in utilization of thermal units is attained from both sources of heat energy which (as pointed out below) is not strictly true.

It is evident that under present conditions the cost of the heat unit produced by the hydroelectric developments in this country cannot compare in cheapness with that obtained by the use of either fuel oil, coal, or coke. It is not altogether fair, however, to compare the efficiency of electric power with that of fuel as a heating source on the basis of

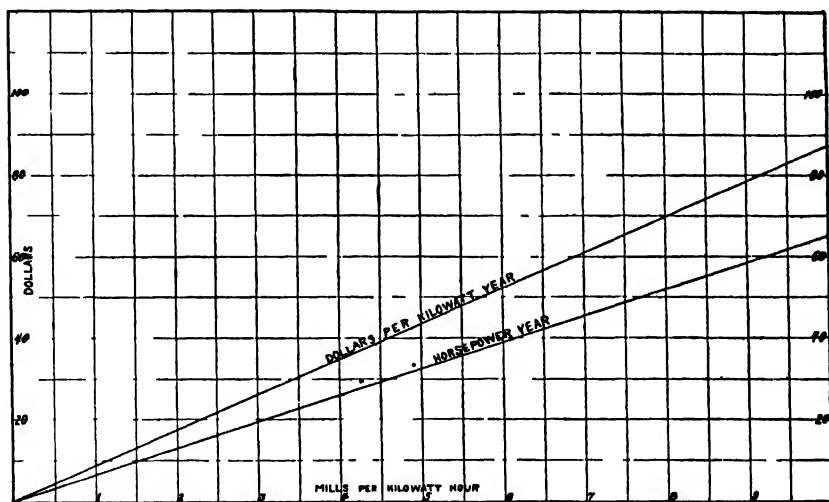


FIG 47—Chart for Converting Power Costs from Mills per K. W. Hour to Dollars per K W Year and H P Year

the actual cost of the thermal unit developed by each. In the electric furnace the heat is very much more localized, and there is less loss through radiation, and in the evolved gases, than in a furnace heated by fuel, where excess air must be introduced for combustion. By proper regenerative apparatus and means of utilizing the sensible heat in the effluent gases, however, this latter loss of valuable heat may be materially reduced.

To further offset the greater efficiency of the thermal unit developed by electric energy it must be borne in mind that the utilization of mine-run phosphates depends upon the location of a furnace plant close to the source of the raw material (the phosphate mines), and while certain of the phosphate deposits of Tennessee are sufficiently close to admit

of the transmission of power to the mines from a development such as Muscle Shoals, Alabama, the Florida deposits are far removed from any source of cheap hydroelectric power. Low-priced fuels (either oil, gas, coal or coke), however, are readily available in practically all of the phosphate fields of this country.

With these facts in mind the writers undertook an investigation to determine if complete elimination of phosphoric acid from proper mixtures of phosphate rock, sand, and coke could not be brought about

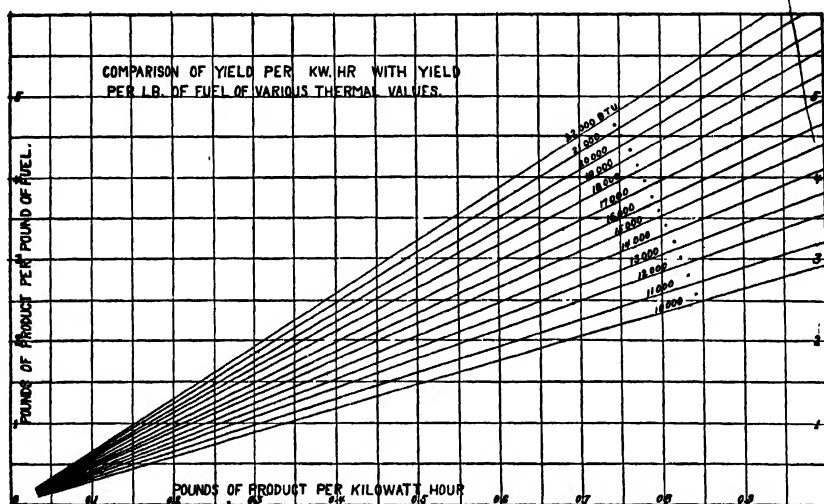


FIG. 48.—Comparison of Yield per K. W. Hour with Yield per Lb. of Fuel of Various Thermal Values.

at the temperatures attained and under the conditions existing in various types of fuel-fired furnaces, and the results have shown that this can be done by properly proportioning the ingredients in the charge and maintaining reducing conditions within the phosphate mass.

Preliminary Laboratory Experiments.

The work was first undertaken on a laboratory scale using relatively pure samples of tricalcium phosphate, quartz flour, and carbon. These ingredients were thoroughly mixed in several proportions, placed in graphite or clay crucibles, and heated in an injection furnace for various periods of time with the crucibles both open and closed. City gas and a cold-air blast were employed in heating these mixtures.

Table XLV shows in part, the results obtained by heating such mixtures with and without the addition of small amounts of aluminum oxide.

TABLE XLV

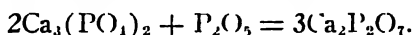
VOLATILIZATION OF PHOSPHORIC ACID FROM MIXTURES OF TRICALCIUM PHOSPHATE, SILICA, COKE, AND ALUMINA, BY SMELTING IN OPEN AND CLOSED CRUCIBLES IN A DENTAL FURNACE USING ILLUMINATING GAS AND AN AIR BLAST

Sample	Crucible	Proportions of Materials Used in Charge				Percentage Composition					Temperature Attained ° C.	Length of Time Elapsed Hours	P ₂ O ₅ in Slag Per Cent	Proportion of P ₂ O ₅ Volatilized Per Cent	Character of Slag
		Ca ₃ (PO ₄) ₂ Grams	SiO ₂ Grams	Al ₂ O ₃ Grams	Coke Grams	SiO ₂ Per Cent	CaO Per Cent	Al ₂ O ₃ Per Cent	P ₂ O ₅ Per Cent	C Per Cent					
12 A...	Closed (clay)	20.0	16.6	...	5.2	40.7	25.9	0.7	21.9	10.8	1,400	0.75	3.24	89.8	Fluid, grayish black
12 G...	Open (clay)	20.0	16.6	...	5.2	40.7	25.9	.7	21.9	10.8	1,400	1	7.20	76.2	Viscous gray; white bloom on surface ^b
12 N ^a ...	Open (graphite)	20.0	16.6	6.6	5.2	35.1	22.4	14.3	18.9	9.3	1,200	1	4.92	80.4	Viscous black
12 N ^b ...	"	20.0	16.6	6.6	5.2	35.1	22.4	14.3	18.9	9.3	1,400	2	None	100.0	Fluid, black
12 O...	Open (clay)	20.0	16.6	...	4.8	41.1	26.2	.7	22.1	9.9	1,400	1	3.36	89.3	Fluid, light gray
12 P...	"	20.0	16.6	6.6	5.0	40.9	26.1	.7	22.0	10.3	1,400	1	2.22	93.0	Fluid, light gray; bloom on surface ^b
12 Q...	"	20.0	16.6	6.6	5.4	40.7	25.8	.7	21.8	11.0	1,400	.75	4.65	84.9	Fluid, light gray; bloom on surface ^b
12 R...	"	20.0	16.6	6.6	5.6	40.5	25.7	.7	21.7	11.4	1,400	.75	2.45	92.2	Fluid, light gray; bloom on surface ^b
12 (1).	"	20.0	16.6	6.6	5.2	40.7	25.9	.7	21.9	10.4	1,300	1	Trace	100.0	Fluid, light gray; large bloom
12 (2).	Closed (clay)	20.0	16.6	6.6	5.2	40.7	25.9	.7	21.9	10.4	1,300	1	Trace	100.0	Fluid, all slag on surface ^b
12 (11)	Open (clay)	20.0	16.6	2.0	5.6	38.7	24.5	5.2	20.7	10.9	1,300	1	5.28	81.3	Viscous light gray; bloom on surface ^b
12 (12)	Closed (clay)	20.0	16.6	2.0	5.6	38.7	24.5	5.2	20.7	10.9	1,300	1	1.91	93.6	Viscous dark; no bloom
12 (15)	Open (clay)	20.0	20.0	2.0	4.8	43.6	23.2	4.9	19.6	8.7	1,300	1	4.26	83.7	Viscous gray; large bloom ^a
12 (16)	Closed (clay)	20.0	20.0	2.0	4.8	43.6	23.2	4.9	19.6	8.7	1,300	1	3.52	86.6	Viscous gray; no bloom
12 (17)	Open (clay)	20.0	22.0	2.0	4.8	45.9	22.2	4.7	18.8	8.4	1,300	1	3.90	84.3	Viscous gray; large bloom ^a
12 (18)	Closed (clay)	20.0	22.0	2.0	4.8	45.9	22.2	4.7	18.8	8.4	1,300	1	3.75	84.8	Viscous gray; no bloom

^a Above.

^b An analysis of the bloom or white crust on the surface of slag obtained in open crucibles shows a considerably higher percentage of phosphoric acid than in the original mixture. The proportion of lime to phosphoric acid coincided very closely with that in calcium pyrophosphate (Ca₂P₂O₇).

An inspection of Table XLV shows that as a rule considerably better results were obtained where the crucibles were kept covered so that the oxidizing gases were not allowed to come in contact with the charge. In most instances where a molten slag was obtained and the heating continued sufficiently long, a very high percentage of the phosphoric acid contained in the charge was volatilized. When the crucibles were left open, however, it was noticed that a thick white crust or "bloom" usually formed over this slag and unless the temperature was raised to the point where the fire-clay crucible itself fused, this crust gave no sign of melting into the slag beneath. The ratio of lime to phosphoric acid in this unfused material conformed closely to the ratio of these ingredients in calcium pyrophosphate. Apparently under the oxidizing conditions existing at the surface of the mass the phosphoric acid distilling from the interior of the charge was fixed at the surface, producing calcium pyrophosphate according to the following equation:



In these preliminary experiments the ratio of silica to lime was approximately 61 to 39, which is very close to the proportions of these ingredients in calcium trisilicate ($\text{Ca}_2\text{Si}_2\text{O}_7$). Charges having this silica lime ratio gave slags from which a quicker and more complete evolution of P_2O_5 was obtained than from those of a less acid nature. Such slags, however, congeal so readily that the tapping of the furnace is rendered somewhat difficult. Subsequent experiments indicate that the more nearly neutral slags are more readily fused and probably better adapted for actual furnace operation.

These experiments pointed conclusively to the importance of maintaining reducing conditions in the phosphate charge, and it appeared at first that the most feasible method of doing so in a mass containing much finely divided material, such as the pebble phosphates of Florida or the mine-run phosphates from Tennessee, was by the indirect heating of the charge so that the oxidizing gases from the burning fuel would not come in contact with the reacting mass until the latter was brought to a molten condition. Accordingly, a fire-brick furnace of semi-commercial size, of the type shown in Figure 49 and described by the senior author and others in United States Patents Nos. 1241971 and 1282994, was constructed at Arlington Experimental Farm, Va. This furnace comprised a central or inner chamber holding about 150 pounds of charge) open both at the top and the bottom but constricted somewhat at the lower end to prevent the charge from working through too rapidly. This chamber was supported by arches of carborundum brick above a hollow hearth intended to receive the molten silicate. The whole was surrounded by an outer chamber into the opposite walls of

which were first set water cooled tuyeres to deliver preheated air for the combustion of the coke as the charge descended upon the hollow hearth. These tuyeres, however, were later replaced by two oil burners so arranged that their flames played upon and around the lower part of the inner chamber, heating the charge by radiation through the $4\frac{1}{2}$ -inch walls. Any fumes which were evolved from the fusing mass were

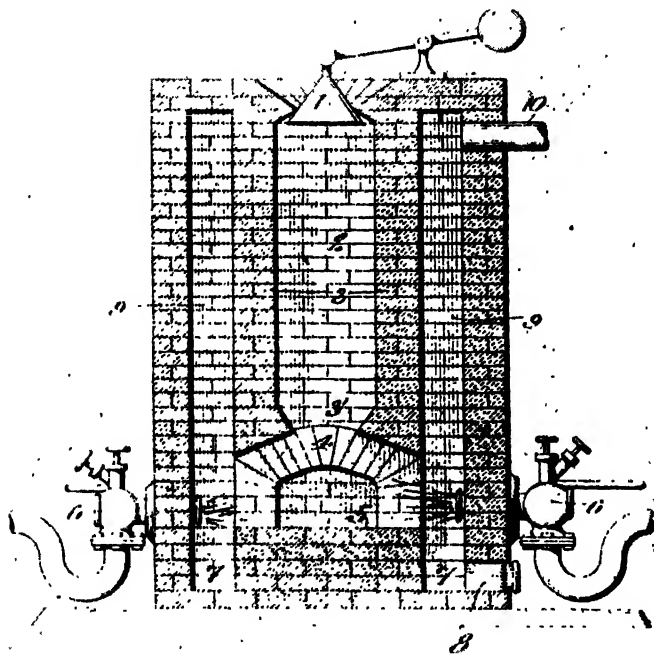


FIG. 49.—Vertical Section of Oil Burning Furnace for the Indirect Heating of Phosphate Charge.

to be drawn down through the charge chamber into the outer chamber and passed, together with the gases of combustion, into the Cottrell precipitator previously described.

This indirect method of heating the charge, however, was so inefficient that after several trials lasting from 18 to 24 hours each, it was abandoned as impractical. Little or no slag was obtained and only a relatively small quantity of phosphoric acid was driven off from the sintered product.

These experiments showed clearly that in order to make the process economically practical the calorific power of the fuel must be more completely utilized, which could only be done by the direct heating of the mass. The most promising type of furnace for this purpose seemed to be a modification of the blast furnace, wherein sufficient coke is used to maintain a reducing atmosphere both in the crucible and in the shaft. The run-of-mine phosphates with which the experiments were being conducted, however, are of such a character that it is impossible to handle them in a plant of the blast-furnace type, because of the large percentage of finely divided material present in the mass, through which it is impossible to force a draft.

The Briquetting of Mineral Phosphates.

Accordingly experiments were undertaken with a view to briquetting the mixtures of finely ground pebble phosphate, sand, and coke, using various binders, such as magnesium chloride, calcium chloride, sodium fluoride, sodium silicate phosphoric acid, acid sludge from the refining of petroleum, sulfite liquor and small percentages of starch. Briquets of several sizes were produced under pressure varying from one-half to 1 ton per square inch, but none of these binders proved entirely satisfactory, either because of their cost or because of the readiness with which the freshly made briquette shattered.

In both Florida and Tennessee, however, certain phosphate deposits in their natural state contain much soft phosphate and claylike material of considerable plasticity, and the binding qualities of some of this run-of-mine phosphate proved sufficiently effective to produce briquettes without the addition of an artificial binder. Such briquettes, however, are usually stronger when freshly made than they are after being dried so in order to insure a furnace charge of the desired mechanical strength, it is wise to employ a small percentage of some binding agent such as sulfite liquor.⁴⁸ Since the binding capacity of this run-of-mine material depends largely on the amount of finely divided material or clay contained therein, the samples obtained from the various phosphate deposits in these two States were ground to 15 mesh in a small grist-mill and then submitted to the mechanical analysis ordinarily employed in the classification of soils. In Table XLVI are given the results of these analyses along with the analysis of very finely ground washed pebble phosphate of the grade used in the production of an average acid phosphate.

⁴⁸ A by-product obtained in the manufacture of paper.

TABLE XLVI

LOCATION, DESCRIPTION, AND MECHANICAL ANALYSES* OF PHOSPHATES USED IN
-BRIQUETTING EXPERIMENTS

Sample No.	Location	Thickness of Stratum	Description	Sand, 1.0-0.05 Milli-meter	Silt, 0.05-0.005 Milli-meter	Clay, 0.005-0.0000 Milli-meter
1	Charleston, S. C., Mining & Manufacturing Co., Fort Meade, Fla.	15 ft. +	Washed pebble phosphate	Per Cent 45.2	Per Cent 36.0	Per Cent 18.8
2	Cumner Lumber Co., Newberry, Fla.	do.	Mine-run phosphate	45.0	21.0	34.0
1-F . . .	Downing Phosphate Co., Bartow, Fla.	do.	56.2	7.6	36.2
1-F (2)	Downing Phosphate Co., near Mulberry, Fla.	20 ft. +	Mine-run pebble phosphate	84.3	5.8	9.9
4-F . . .	do.	do.	do.	78.5	7.2	14.3
1-T . . .	Consolidated Phosphate Co., Hickman County, Tenn.	6 ft.	Brown phosphate containing lump rock	73.3	14.6	12.1
3-T . . .	Deposit near Gallatin, Tenn.	4 ft.	Brown disintegrated phosphate	54.1	18.3	27.6
4-T . . .	do.	do.	Similar to No. 3-T	55.4	17.6	27.0
6-T . . .	Ruhm Phosphate Co., Mount Pleasant, Tenn.	5 ft.	Brown phosphate containing lump rock	66.2	16.1	17.7
7-T . . .	do.	7 ft.	do.	59.0	16.8	24.2
8-T . . .	do.	14 ft.	Sample from upper end of waste pond	42.5	39.0	18.5
9-T . . .	do.	15 ft.	Sample taken 63 ft. from 8-T	24.2	50.2	25.6
10-T . . .	do.	10 ft. 3 in.	Sample taken 63 ft. from 9-T	30.4	45.8	23.8
11-T . . .	do.	5 ft. 11 in.	Sample taken 63 ft. from 10-T	11.6	56.7	31.7
12-T . . .	do.	5 ft.	Sample taken 63 ft. from 11-T	22.5	41.1	34.4
13-T . . .	do.	4 ft. 6 in.	Sample taken 63 ft. from 12-T	7.2	44.0	48.8
14-T . . .	Charleston (S.C.) Mining Co., Wales, Tenn.	10 to 20 ft.	Brown disintegrated phosphate	50.4	20.4	29.2
15-T . . .	International Agricultural Corp., Wales, Tenn.	10 to 20 ft.	High-grade disintegrated phosphate	51.6	18.4	30.0
16-T . . .	do.	do.	Low-grade disintegrated phosphate	53.7	13.8	32.5
18-T . . .	Federal Chemical Co., Ridley, Tenn.	6 to 10 ft.	Mine-run brown phosphate	46.5	19.7	33.8
19-T . . .	do.	do.	do.	62.4	16.6	21.0
20-T . . .	do.	do.	do.	52.6	22.4	25.0

* Mechanical analyses made according to the method employed in this bureau for the classification of soils.

It will be noticed that with few exceptions all of the samples of run-of-mine phosphates contained in their natural state much higher percentages of very finely divided material or clay than the high-grade washed pebble phosphate (Sample No. 1), even though the latter was ground in a ball mill for a considerable length of time. While most of these samples would yield excellent briquets when 7 to 10 per cent of water was added and the material submitted to a pressure of from one-half to one ton per square inch, the ultimate mechanical compo-

TABLE XLVII

PARTIAL CHEMICAL ANALYSIS AND SILICA-LIME RELATIONS OF NATURAL PHOSPHATES

Sample No.	Chemical Analysis						Ratio, SiO ₂ : CaO	Quantity of Sand or High-Grade Rock to Be Added to 100 Parts of Material to Give Ratio SiO ₂ :CaO = 59.0:41.0 = 1.439	
	SiO ₂	CaO	P ₂ O ₅	Fe ₂ O ₃	Al ₂ O ₃	Total		Sand	Rock
	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent		Parts	Parts
1*.....	6.85	44.78	31.09	1.48	2.13	86.33	0.153	57.36
2.....	32.79	26.47	21.43	...	^b 11.78	92.47	1.239	5.00
1-F.....	26.96	29.05	23.61	2.09	8.40	90.11	.928	14.85
1-F (2).....	37.57	29.70	21.52	...	^b 3.92	92.71	1.265	5.20
4-F.....	45.20	24.29	18.36	...	^b 4.91	92.76	1.861	17.70
1-T.....	10.00	42.66	31.86	3.26	3.90	91.68	.232	51.35
3-T.....	30.23	28.17	22.03	4.06	6.94	91.43	1.073	10.27
4-T.....	38.74	23.00	17.88	4.45	5.00	89.07	1.686	8.20
6-T.....	15.53	38.32	27.68	3.56	4.33	89.42	.405	39.65
7-T.....	18.69	33.09	25.20	4.84	5.54	87.36	.565	28.91
8-T.....	49.60	18.24	14.21	3.76	4.73	90.54	2.717	33.9
9-T.....	58.94	12.20	10.23	4.30	5.06	90.73	4.830	60.1
10-T.....	56.32	15.16	12.05	3.98	4.41	91.92	3.716	50.0
11-T.....	66.81	8.05	6.92	4.46	6.82	93.06	8.300	80.0
12-T.....	55.68	12.58	10.51	4.78	7.85	91.40	4.430	54.5
13-T.....	61.18	6.60	6.32	5.68	9.57	89.34	9.275	74.8
14-T.....	23.42	30.78	22.70	5.22	7.40	^b 89.52	.762	20.85
15-T.....	22.26	31.41	23.85	4.78	7.79	90.09	.708	22.94
16-T.....	57.34	12.00	11.23	4.90	7.23	92.70	4.775	58.0
18-T.....	23.86	30.26	22.76	4.55	8.40	89.83	.788	19.64
19-T.....	16.50	37.41	25.84	3.02	5.50	88.27	.441	37.33
20-T.....	28.90	28.64	20.79	3.82	6.63	88.78	1.070	12.31

* This phosphate was used in reinforcing the lower grades of mine-run material.

^b Combined oxides of iron and aluminum.

sition of a charge suitable for furnace treatment depends upon the amount of sand or higher grade phosphate which must be added to give the proper silica-lime ratio for the evolution of phosphoric acid at high temperatures. In Table XLII are given the chemical analyses of these samples and the quantities of sand or high-grade rock which must be added to give a silica-lime ratio of 59 to 41, which was the proportion used in the earlier work conducted on a semi-commercial scale.

An inspection of Table XLVII will show that samples Nos. 4-F, 4-T, 8-T, 9-T, 10-T, 11-T, 12-T, 13-T, and 16-T are so low in phosphoric acid as to eliminate them as commercial possibilities, unless they are reinforced with higher grade phosphates. But most of these samples (8-T to 13-T, inclusive) were taken from the waste pond of an old phosphate plant and represent the detritus washed out from run-of-mine material in preparing a high-grade rock for the market. It will also be noticed that in most instances where the phosphate content of the samples is low and the silica content high, there is sufficient clay present to admit of adding enough higher grade phosphate rock to obtain the proper silica-lime ratio without substantially reducing the binding qualities of the resultant mixture.

In Table XLVIII are given the quantities of sand and coke which were added to 100 parts of the better grades of mine-run phosphate to

TABLE XLVIII

BRIQUETTES FORMED BY MIXTURES OF NATURAL PHOSPHATE ROCK, SAND, AND COKE

Sample No.	Briquette Mixture SiO ₂ CaO 59:41			Calculated composition of briquette Mixture (Air-dried)					
	Rock Sample	Sand	Coke	SiO ₂	CaO	P ₂ O ₅	Fe ₂ O ₃	Al ₂ O ₃	Coke *
	Grams	Grams	Grams	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
2	100	5.00	14.32	31.67	22.18	17.96	^b 9.87	12.00
1-F	100	14.85	15.65	32.10	22.25	18.10	1.60	6.44	12.00
1-F (2) ..	100	5.20	14.35	35.79	24.84	18.00	^b 3.29	12.00
3 T	100	10.27	15.05	32.31	22.47	17.60	3.24	5.54	12.00
5-T	100	20.41	16.40	32.80	22.80	17.62	3.00	4.75	12.00
7 T	100	28.91	17.55	32.70	22.59	17.20	3.31	3.78	12.00
14-T	100	20.85	16.47	32.25	22.40	16.54	3.80	5.39	12.00
15 T	100	22.94	16.75	32.35	22.50	17.09	3.42	5.58	12.00
18 T	100	19.64	16.30	32.00	22.23	16.75	3.35	6.18	12.00

* The fixed carbon plus ash considered as coke. The coke used in these experiments contains 14.9 per cent of ash. An analysis of this ash showed that the coke in the briquetted mixture adds 0.98 per cent SiO₂, 0.02 per cent CaO, and 0.63 per cent Al₂O₃, Fe₂O₃ to the mix.

^b Combined oxides of iron and aluminum.

make up charges suitable for furnace treatment. The composition of these briquetted charges is given in the last six columns of this same table. In Table XLIX these same data are given for mixtures of two or more samples of mine-run phosphate and the figures show how many low-grade deposits may be utilized by mixing the material with that from near-by or adjacent deposits of higher grade.

Subsequent work on a larger scale, however, has proven that the briquetted charge can be made more nearly neutral or actually somewhat basic in so far as the relation of lime to silica is concerned. This is very important from the standpoint of economy since it means less charge need be smelted per unit of P_2O_5 recovered.

TABLE XLIX

BRIQUETTES FORMED BY MIXTURES OF HIGH GRADE AND LOW GRADE PHOSPHATE ROCK WITH COKE

Sample No	Briquette Mixture SiO_2 CaO = 59.41			Calculated composition of briquette Mixture (Air-dried)					
	Rock Sample	Sand	Coke	SiO_2	CaO	P_2O_5	Al_2O_3	Fe_2O_3	Coke *
	Grams	Grams	Grams	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
4-F	44.4	}	13.63	36.04	24.01	17.69	3.84	..	12.00
1-F (2) ..	55.6								
3-T	35.48		13.63	31.42	20.92	17.00	3.80	5.00	12.00
4-T	64.52								
7-T	44.7		13.63	31.50	21.90	16.83	3.74	4.49	12.00
8-T	55.3								
15-T ..	63.6		13.63	30.80	21.45	16.95	4.25	6.68	12.00
16-T	36.4								
18-T	33.3								
19-T	33.3		23.10	33.00	22.95	16.55	4.89	6.37	12.00
20-T	33.3								

* The fixed carbon plus ash considered as coke. The coke used in these experiments contains 14.9 per cent of ash. An analysis of this ash showed that the coke in the briquetted mixture adds 0.98 per cent SiO_2 , 0.02 per cent CaO, and 0.63 per cent Al_2O_3 , Fe_2O_3 to the mix.

^b Al_2O_3 , Fe_2O_3

In preparing the samples for briquetting purposes it was found that a Sturtevant hammer mill would grind run-of-mine phosphate containing as high as 10 per cent of moisture, to 15 mesh without clogging the mill. From a commercial standpoint this is a very important item, since much of the material as it comes from the mines contains a high percentage of moisture, the complete removal of which is somewhat costly. Moreover, since the presence of from 7 to 10 per cent of moisture in the final mixture is necessary in order to give the material the

proper plastic qualities for briquetting purposes, it would be unfortunate to have to dry the phosphate only to wet it again in order to briquet it. It has been found unnecessary to grind the phosphate finer than that which will go through a sieve having 15 meshes to the linear inch, although finer grinding aids somewhat in imparting greater re-



FIG. 50.—Small Briquetting Press Used in Making up Furnace Charge.

sisting power to the briquettes and probably accelerates slightly the rate of the reactions in the furnace.

The briquetting machine of semi-commercial size used in preparing the phosphate charges for furnace treatment is illustrated in Figure 50.

In Tables L and LI are given the results of the shatter and compression tests on briquettes made from mixtures of relatively high-grade phosphate, sand, and coke, as well as those on briquettes made up of

TABLE L
SHATTER TESTS ON BRIQUETTES MADE FROM NATURAL PHOSPHATE ROCK,
SAND, AND COKE

Sample No.	Fresh Briquettes			Air-Dried Briquettes *			Oven-Dried Briquettes	
	Weights	H ₂ O	Shat-tered on Drop-ping to Cement Floor	Shat-tered on Drop-ping to Cement Floor	With-stood Drop on Mass of Similar Briquets	Com-pression Test	Shat-tered on Drop-ping to Cement Floor	With-stood Drop on Mass of Similar Briquets
	Grams	Per Cent	Feet	Feet	Feet	Pounds per Sq. In.	Feet	Feet
1-F.....	107.0	11.21	5	4	6	14
1-F.....	105.5	13.53	10	5	9	16
1-F.....	108.7	13.45	20 +	8	20
2.....	110.0	10.00	20 +	7
3-T.....	133.5	8.69	4	5	18	472	9	20
3-T.....	124.7	11.15	8	6	20	800	10	20
3-T.....	115.2	13.63	14	7	20	838	12	20
5-T.....	113.7	11.08	8	7	20	483	11	20
5-T.....	126.4	13.13	12	8	20	654	12	20
7-T.....	122.1	10.49	..	5	7	20
7-T.....	105.2	9.50	8	6	15	815	9	20
7-T.....	116.4	13.14	10	7	16	950	12	15
14-T.....	131.3	9.90	9	6	18	724	9	20
14-T.....	120.9	10.47	12	6	18	793	10	20
15-T.....	121.7	9.53	6	8	20	407	11	20
15-T.....	119.2	12.35	20	7	20	894	13	20
15-T.....	115.7	12.62	12	11	20	538	10	20
18-T.....	120.6	13.27	20 +	8	20	887	13	20

* Average weight = 109 grams. Average H₂O content 2.95 per cent.

TABLE LI
SHATTER TESTS ON BRIQUETTES MADE FROM MIXTURES OF LOW-GRADE AND HIGH-GRADE PHOSPHATE ROCK WITH COKE

Sample No.	Fresh Briquettes			Air-Dried Briquettes			Oven-Dried Briquettes	
	Weights	H ₂ O	Shat-tered on Drop-ping to Cement Floor	Shat-tered on Drop-ping to Cement Floor	With-stood Drop on Mass of Similar Briquets	Com-pression Test	Shat-tered on Drop-ping to Cement Floor	With-stood Drop on Mass of Similar Briquets
	Grams	Per Cent	Feet	Feet	Feet	Pounds per Sq. In.	Feet	Feet
3-T.....	118.5	12.00	12	12	18	728	14	20
4-T.....								
7-T.....								
8-T.....	113.5	11.90	8	8	20	738	8	20
7-T.....								
8-T.....								
8-T.....	103.0	14.30	10	10	20	960	10	20
15-T.....								
16-T.....								
18-T.....	111.6	14.35	20 +	10	20	1,004	18	20
19-T.....								
20-T.....								
20-T.....	121.6	11.02	9	8	15	811	11	20
20-T.....								
20-T.....								

mixtures of two or more phosphates. The briquettes were made up with varying percentages of moisture and the shatter and compression tests were applied not only to the freshly made briquettes but also to the air-dried and oven-dried samples.

With few exceptions all of the briquettes in the air-dried condition withstood a drop on a cement floor of from 6 to 8 feet and a drop of 20 feet or more upon a mass of other briquettes.

Through the courtesy of two commercial firms, briquetted charges of several tons were made up with the silica-lime ratio given in the preceding tables and protracted tests made on a semicommercial scale in a modified form of blast furnace which is described later.

Effect of High Temperatures on Various Briquetted Mixtures.

The results obtained in these larger scale experiments indicated that the silica-lime ratio as well as the carbon content of the briquetted charge might be advantageously altered to give a somewhat more rapid evolution of phosphoric acid without sacrificing the fluidity of the slag. Accordingly a series of laboratory experiments was undertaken to determine the following points: (1) The percentage of coke to incorporate in the briquettes for optimum reducing effect; (2) the optimum silica content required for the rapid elimination of phosphoric acid and the production of a fluid slag; (3) the most practical temperature to employ to effect the decomposition of the phosphate without undue erosion of the refractory lining of the furnace.

Four batches of briquettes were made up of run-of-mine phosphate from Tennessee mixed with sufficient sand to give the following ratios of silica to lime in the charge—59:41, 61:39, 63:37 and 68:32. The amount of coke in the first batch of briquettes (having the lowest silica content) varied between 12 and 15 per cent of the weight of the charge, and in certain briquettes bituminous coal was substituted for coke, this coal being added in sufficient quantity to supply 10 per cent of fixed carbon to the mass. After a number of tests, however, it appeared that 14 per cent of coke was ample to give the proper reducing reaction and this amount was used in the three other batches of briquettes where higher proportions of silica were employed.

In these experiments the same type of small injector gas furnace was used as that employed in the preliminary work where pure mixtures of tricalcium phosphate, silica and carbon were smelted, but in order to obtain somewhat higher temperatures than previously employed, the air for the combustion of gas was passed through a steel coil heated by two Bunsen burners. The air was thus preheated to a temperature of 250° C.

The results of these experiments are shown in detail in Table LII.

TABLE LII

TIME AND TEMPERATURE REQUIRED FOR THE VOLATILIZATION OF PHOSPHORIC ACID FROM BRIQUETTED CHARGES OF PHOSPHATE ROCK, SAND, AND COKE CONTAINING DIFFERENT RATIOS OF CaO to SiO₂

Sample No.	Composition of Briquettes (Exclusive of Carbon)					Coke	Silica- Lime Ratio, SiO ₂ : CaO	Time of Fusion	Tem- pera- ture	P ₂ O ₅ in Slag	P ₂ O ₅ Volat- ilized	Character of Slag
	SiO ₂	CaO	P ₂ O ₅	Fe ₂ O ₃	Al ₂ O ₃							
	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent							
50, 81	37.9	26.4	18.1	4.1	4.6	Per 14	50:41	20	1,600	4.93	Per 76.4	Liquid, dark, glassy, translucent, small amount pyrophosphate.
49, 90	37.9	26.4	18.1	4.1	4.6	14	50:41	25	1,595	4.33	79.4	Do.
57, 48	37.9	26.4	18.1	4.1	4.6	12	50:41	30	1,575	6.77	66.8	Liquid, bluish, glassy, slight opalescence, no pyrophosphate.
83	37.9	26.4	18.1	4.1	4.6	15	50:41	30	1,580	4.00	81.0	Liquid, dark, glassy, translucent, small amount pyrophosphate.
75, 83, 88, 101	37.9	26.4	18.1	4.1	4.6	14	50:41	30	1,610	2.65	87.6	Very liquid, light, glassy, translucent, very small amount pyrophosphate.
85, 86	37.9	26.4	18.1	4.1	4.6	14	50:41	35	1,605	1.18	94.6	Very liquid, light, glassy, translucent, no pyrophosphate.
40	37.9	26.4	18.1	4.1	4.6	12	50:41	40	1,590	2.5	88.4	Liquid, light, glassy, translucent, no pyrophosphate.
108, 100	37.9	26.4	18.1	4.1	4.6	14	50:41	40	1,640	1.63	92.5	Very liquid, light, glassy, translucent, no pyrophosphate.
56	37.9	26.4	18.1	4.1	4.6	15	50:41	50	1,500	1.08	95.0	Very liquid, dark, glassy, translucent, no pyrophosphate.
57, 82	37.9	26.4	18.1	4.1	4.6	10	50:41	20	1,570	6.17	70.0	Liquid, black, glassy, translucent, no pyrophosphate.
99	37.9	26.4	18.1	4.1	4.6	10	50:41	25	1,595	3.16	85.1	Liquid, dark, glassy, translucent, no pyrophosphate.
74, 78	37.9	26.4	18.1	4.1	4.6	10	50:41	30	1,615	.57	97.4	Very liquid, light, glassy, translucent, no pyrophosphate.
68, 113	40.0	25.6	17.5	4.0	4.5	14	61:39	20	1,595	6.85	65.0	Liquid, bluish, glassy, slight opalescence, large amount pyrophosphate.
92, 104	40.0	25.6	17.5	4.0	4.5	14	61:39	25	1,585	4.62	77.0	Do.

76, 87	40.0	25.6	17.5	4.0	4.5	14	61:39	30	1.615	1.25	94.1	Liquid, dark, glassy, translucent, no pyrophosphate.
71	40.0	25.6	17.5	4.0	4.5	14	61:39	35	*1.610	.11	99.5	Slightly viscous, dark, glassy, slightly crystalline, no pyrophosphate.
70, 79	42.0	24.7	17.0	3.8	4.3	14	63:37	20	1.605	.581	69.6	Liquid, bluish, glassy, translucent, medium amount pyrophosphate.
93, 94	42.0	24.7	17.0	3.8	4.3	14	63:37	25	1.610	3.12	84.1	Viscous, bluish, glassy, slight opalescence, medium amount pyrophosphate.
67, 77, 84	42.0	24.7	17.0	3.8	4.3	14	63:37	30	1.610	.52	97.4	Viscous, light, glassy, translucent, small amount pyrophosphate.
72	42.0	24.7	17.0	3.8	4.3	14	63:37	35	*1.610	.12	99.4	Viscous, dark, glassy, translucent, small amount pyrophosphate.
106	47.8	22.3	15.3	3.5	4.0	14	68:32	20	1.590	4.04	76.5	Viscous, blue, glassy, opalescent, large amount pyrophosphate.
95	47.8	22.3	15.3	3.5	4.0	14	68:32	25	1.585	2.14	87.8	Do.
97, 98	47.8	22.3	15.3	3.5	4.0	14	68:32	30	1.610	.50	97.2	Viscous, bluish, glassy, slight opalescence, medium amount pyrophosphate.
111	47.8	22.3	15.3	3.5	4.0	14	68:32	35	1.640	.22	98.8	Very viscous, dark, glassy, translucent, small amount pyrophosphate.
110	47.8	22.3	15.3	3.5	4.0		68:32	40	1.630	.21	98.9	Do.

* Estimated temperature. ^b Coal.

The data given in the above table show that, on the whole, an increase in the silica content of these briquetted mixtures resulted in a more rapid evolution of phosphoric acid, but usually at the sacrifice of the fluidity of the slag.

The ratios of silica to lime in the first and third batches of briquettes --namely, 59:41 and 63:37--do not correspond to any definite calcium silicates, but the proportions of these two ingredients (61:39 and 68:32) in the second and fourth batches coincide closely to the ratios of silica to lime in calcium trisilicate ($\text{Ca}_2\text{Si}_2\text{O}_7$) and calcium di-meta silicate (CaSi_2O_6) respectively.

Where the proportion of silica to lime was 59:41 (first batch of briquettes) it required from 40 to 50 minutes to drive off the phosphoric acid from the charge at a temperature of $1,600^\circ \text{C}$. In every other instance, however (where the silica content was higher), the nearly complete volatilization of phosphoric acid was accomplished in from 30 to 35 minutes. Yet the slight increase in the rate of evolution of P_2O_5 where the proportion of silica to lime was raised above that in the second batch of briquettes (namely, 61:39) was insufficient to offset the disadvantages of having a more viscous slag to tap and a greater weight of charge to smelt.

Another important point brought out by these experiments is the possibility of using bituminous coal as a reducing agent in the briquettes in lieu of coke. Not only was it found that the evolution of the volatile hydrocarbons which are given off in the preliminary heating of such mixtures did not disintegrate or split the briquettes but that there was an actual deposition of carbon (from the decomposition of hydrocarbons) throughout the mass which seemed to aid in the subsequent reduction of the phosphate mineral.

In the following chart (Figure 51) the rate of volatilization of P_2O_5 from briquettes of various compositions is graphically illustrated by curves.

The Larger Scale Experiments.

With the exception of a few experiments conducted in the furnace shown in Figure 49, practically all of the larger scale work on the volatilization of phosphoric acid from briquetted charges of phosphate rock, sand, and coke have been conducted in furnaces having certain features of both the open-hearth and blast-furnace types. While the dimensions of the furnace proper, the materials used for linings, and the character of the outer shell were altered from time to time, the furnace plan throughout the experiments has been in a general way the same. Briefly, this furnace consisted of an elongated arched crucible, 12 feet in length, 2 feet in diameter, and 2 feet in height at

the crown of the arch. In the center of the arched roof of this chamber was a circular opening leading up into a shaft or charge chamber 7 feet 6 inches in height and having the shape of the usual type of blast furnace. The throat of the chamber where it discharged onto the furnace hearth was originally 12 inches in diameter, but this was later

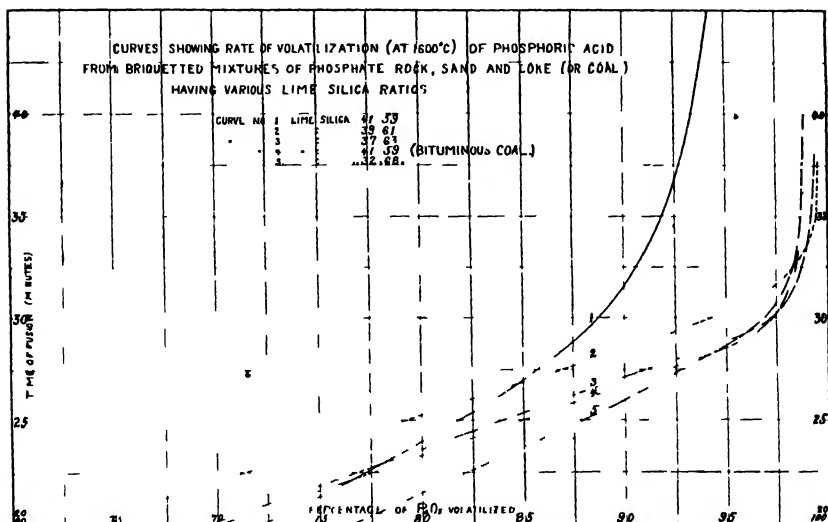


FIG. 51 Curves Showing Rate of Volatilization of Phosphoric Acid from Briquetted Mixtures of Phosphate Rock, Sand, and Coke Having Various Lime Silica Ratios

reduced to 10 inches. This charge chamber widened out gradually until at the top of the bosh the internal diameter was 2 feet. From here on the walls of the chamber tapered inwardly until at the top of the shaft the opening was only 14 inches in diameter. This chamber held approximately 700 pounds of briquetted charge. One foot from the top of the furnace shaft was a flue leading into a dust chamber, which in turn led to a main from which the gases entered the stoves. These stoves (four in number) were of the two pass type and consisted of steel shells 4 x 10 feet lined with fire brick. The furnace was originally constructed entirely of fire brick, but after a number of experiments it was found that the temperatures attained were so high (1500° to 1700° C.) that it was desirable to replace them in part by carborundum brick.

The furnace shaft and crucible were steel jacketed and in the final installation they were water cooled. Two water cooled oil burners at

either end of the elongated crucible were employed to furnish the necessary fuel, and preheated air for its combustion was introduced at these same points, a positive pressure blower being used to deliver the air at a pressure of from 1 to 4 pounds per square inch through a 6-inch main. The molten slag was tapped from two water cooled cinder notches.

From the stoves the burned gases containing P_2O_5 entered a 6-inch main and thence through a cooler into the lower header of a Cottrell precipitator which consisted of 9 terra cotta tile pipes 6 inches in diameter and 14 feet long. The discharge electrodes in these pipes were



FIG. 52—General View of Fuel Fired Furnace and Auxiliary Equipment Wherein the First Large Scale Experiments Were Conducted

of 14 gauge monel metal wire to which were hung individual lead weights which in turn were fastened to a rigid grid to prevent oscillations of the wires.

Views of this plant and its auxiliary equipment are shown in Figures 52-55.

Six tests lasting from $5\frac{1}{2}$ to 70 hours (after the furnace had been brought up to the desired temperature) were conducted in this furnace and over 7 tons of briquettes smelted down to a molten slag.

While some of these tests were far from satisfactory owing chiefly to mechanical difficulties, the results have demonstrated conclusively that it is feasible to drive off phosphoric acid nearly completely from

briquetted charges of phosphate rock, sand, and coke in large-scale operations by means of burning fuel.

Volatilizations of P_2O_5 varying from 50 to 97 per cent were obtained and when operating conditions permitted this was collected as strong phosphoric acid by means of the Cottrell electrical precipitator.

It has also been shown that by the use of high-grade refractories and proper water-cooling devices a furnace can be constructed which will withstand the combined effects of siliceous slags and the high temperatures (1500° to 1650° C.) attained in this process.



FIG. 53.—A Close View of the First Oil Burning Furnace for the Volatilization of Phosphoric Acid.

Other points brought out by these experiments are the feasibility and advantages of having auxiliary equipment for heat regeneration and to make sure that only oxidized products are transmitted to the electrical precipitator where the phosphoric acid is collected.

In this furnace, however, the relatively short shaft or charge chamber made it necessary to localize or concentrate the highest temperature upon the furnace hearth. During the last protracted test (of 70 hours), the impurities present in the oil frequently made it necessary to operate the burners at a rather high pressure caused a greater fuel consumption than was either essential or desirable, since it resulted in a long flame

which burned well up in the shaft causing the entire charge to soften and settle down upon the hearth in a semifluid condition. The lower levels of this viscous slug therefore were not exposed to the maximum temperature for a sufficient time to drive off the phosphoric acid either rapidly or completely. In a furnace of larger dimensions with a higher

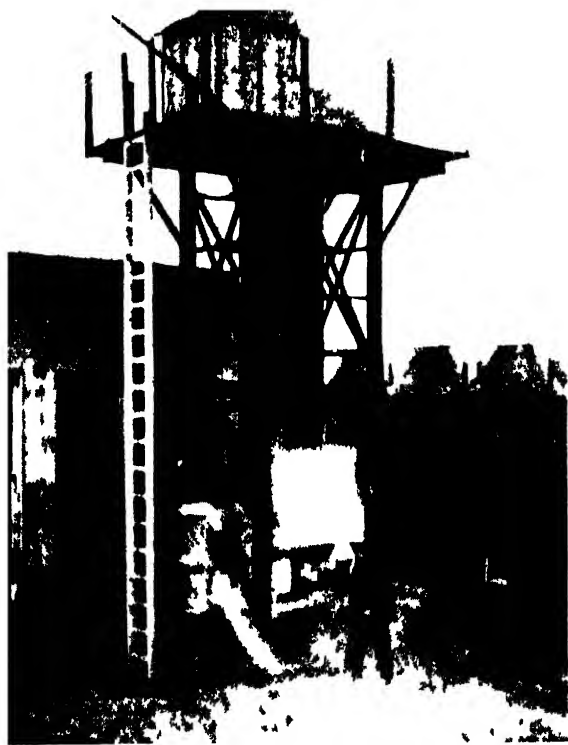


FIG. 54. Cottrell Electrical Precipitator Electric Current Was Turned On

shaft and where much greater air pressures are employed (such as in the ordinary blast furnace) trouble of this kind is not encountered, since the charge while descending through the shaft is exposed to the necessary high temperatures for a considerably longer period than is possible in a plant of the size employed in these experiments.

For the efficient working of such a furnace it is also essential to

eliminate the shutdowns such as are necessitated by the failure of the blowing equipment. The ratio of surface area to the volume of this furnace was such that radiation losses were far more serious than in a plant of large capacity. Even fluctuations in the amount of in de-

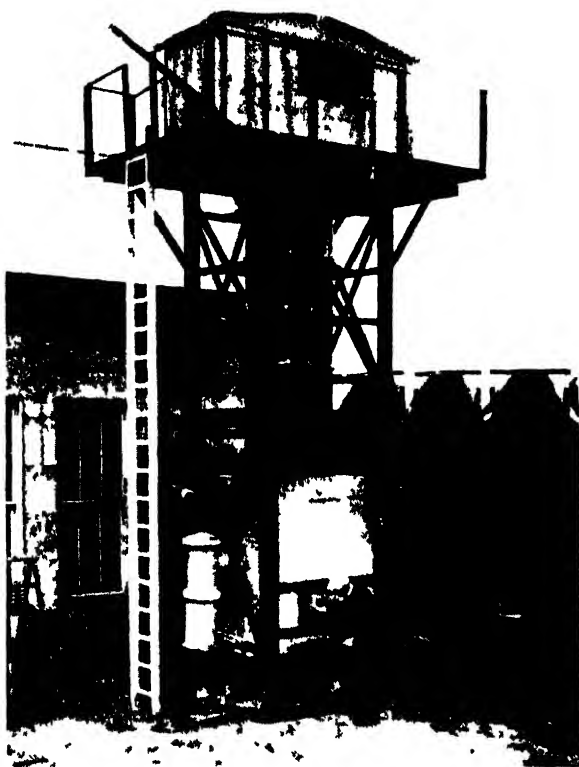


FIG. 55. Cottrell Precipitator. Picture Taken Two Minutes after Current Was Thrown On. Tubes of P.O. Being Collected.

livered are apt to cause the formation of scaffolds in the shaft which further upset the relation between the oil and the air required for its combustion. Because of the small diameter of the furnace shaft, a scaffold often meant a complete bridging over of the charge, which put an added load on the blower to force the air through this partially fused mass. While scaffolds also form at times in large blast furnaces,

the complete bridging over of the charge seldom occurs in normal operation, and if so may often be remedied by a momentary reduction in the air pressure.⁴⁹

This process (somewhat modified) is now being tried out in a small commercial way by the Victor Chemical Works near Chicago, Illinois, but in view of the fact that this concern has done much of the pioneer work in its development, it does not care to have its results generally known, the data therefore are not yet available for publication. Suffice it to say that while a number of problems arose in adapting this process to a commercial installation which were not encountered or foreseen in the experimental unit at Arlington, Va., the ultimate success of the fuel furnace method of producing phosphoric acid now seems practically assured.

Estimated Cost of Production.

The cost of producing phosphoric acid and soluble phosphates by the fuel furnace method must yet be to a large extent estimated since refinements in the process and the utilization of by-products have not been fully worked out. While it is doubtful whether soluble P_2O_5 for fertilizer purposes can be produced more cheaply by this process from high-grade phosphate rock than by the sulfuric acid method, by employing run-of-mine phosphates and locating a plant at or near the source of this raw material the furnace process should have a distinct advantage over the older method.

During the tests just described, however, there were periods of from three to five hours when the furnace appeared to operate quite efficiently, and if the data taken at such times are considered indicative of normal working conditions, the cost of producing phosphoric acid by this method appears economically superior to that which is now almost universally employed.

Probably, if all the factors are considered, the fairest and at the same time some of the most favorable figures showing the ratio of oil consumed to the yield of product were obtained during the latter part of the 20-hour test begun on October 8, 1920. The cost data given below therefore are largely based on these results, and while it is assumed that the operation be conducted on a larger scale in a furnace with an average daily output of 30 tons of P_2O_5 , the fuel consumption per ton of P_2O_5 produced is that actually determined in the last three

⁴⁹ Johnson, J. F., Jr., *The Principles, Operation, and Products of the Blast Furnace*, pp. 348-349 (1918); Wilcox, F. H., *Bul. 130, Bureau of Mines*, pp. 188, 250-252 (1917).

and a half hours of this test with the Arlington furnace. In Table LIII is given the estimated cost of mine-run phosphate briquetted and ready for furnace treatment, in Table LIV the cost of producing 1 ton (2,000 pounds) of P_2O_5 from this briquetted charge is shown, and in Table LV the cost of manufacturing available phosphoric acid by treating high-grade washed phosphate rock with the liquid phosphoric acid thus produced is given.

TABLE LIII

QUANTITIES AND ESTIMATED COST OF MINE-RUN PHOSPHATE AND COKE BRAIZE REQUIRED PER TON OF P_2O_5 , AND COST OF BRIQUETTING THIS MIXTURE FOR FURNACE TREATMENT

Charge and Its Manipulation for Furnace Treatment	Quantity	Cost—	
		Per Ton of Material	Per Ton of P_2O_5
	Pounds		
Mine-run phosphate and sand.....	10,542
Mining	10,542	\$0.75	\$3.53
Drying	10,542	.25	1.18
Grinding25	1.18
Coke braize	1,716	5.00	4.29
Grinding	1,716	.50	.40
Mixing and briquetting.....	12,258	1.25	7.66
Total.....	8.00	18.24

TABLE LIV

ESTIMATED COST PER TON OF PHOSPHORIC ACID (P_2O_5), 90 PER CENT YIELD, PRODUCED BY SMELTING BRIQUETTED CHARGES OF MINE-RUN PHOSPHATE IN AN OIL-BURNING FURNACE

Items	Cost	Items	Cost
Briquetted material	\$18.24	Labor of 18 men, at \$5 per day	\$ 3.00
Fuel oil, 360 gallons, at 2 cents per gallon	7.20	Insurance50
Power	3.50	Overhead expenses	1.50
Interest on \$100,000, at 6 per cent55	Total cost per ton.....	36.31
Depreciation on \$100,000, at 20 per cent	1.82	Total cost per unit.....	.36

TABLE IV

ESTIMATED COST OF PRODUCING ONE TON OF AVAILABLE PHOSPHORIC ACID (P_2O_5) IN THE FORM OF DOUBLE SULFATE BY TREATING HIGH GRADE PHOSPHATE ROCK WITH PHOSPHORIC ACID OBTAINED BY THE FUEL FURNACE PROCESS

Item	Quantity	Cost—	
		Per Ton of Material	Per Ton of Product
Phosphate rock (washed)	108 tons	\$ 3 50	\$ 3 43
P_2O_5 in form of 58 Be acid	* 67	36 31	24 35
Labor and power		1 1 30	2 68
Drying		1 25	52
Total cost per ton P_2O_5		—	30 98
Total cost per unit P_2O_5			31

* Equivalent to 108 tons of H_2PO_4 (58 Be)

¹ Cost per ton of material handled

By comparing the figures given in Tables I IV and I V with those in Tables XXXVII to XLII it will be seen that the estimated cost per ton (or per unit) of P_2O_5 produced by the fuel furnace method is considerably below that obtained by either the electric furnace or sulfuric acid process. If the acid thus produced be used in the manufacture of double acid phosphate the economy of this method appears even more marked.

Chapter 8.

Phosphate Baking Acids and Powders.

Next to the fertilizer industry the most important and largest consumer of bone and phosphate rock is the baking powder industry.

The practice of using a leavening agent in order to produce the aeration or lightness so desirable in bread, cakes and pastries dates back to the earliest times. It was known to the Egyptians, handed down by them to the Greeks and from the Greeks to the Romans.¹ Both leavened and unleavened bread are mentioned in the Bible.

The first leavening agent employed was some form of yeast or ferment which acts on the carbohydrates in the flour, producing alcohol and carbon dioxide. The latter fills the dough with innumerable little gas cells and when the bread is baked the gas in these cells expands, puffing up the loaf and giving it the desired lightness and palatability.

Later when the nature of carbon dioxide and the part it plays in the leavening process was better understood certain definite chemical compounds were substituted in part for the living organisms (yeast) as means of generating carbonic acid.

At one time (and even now to a limited extent) bicarbonate of soda (baking soda) alone was commonly employed for baking purposes, the heat of the oven being depended upon to decompose this salt into carbon dioxide and normal sodium carbonate. On account of the alkaline nature of the latter compound, however, the yellow color of the resultant product, and the somewhat unpleasant taste which it imparts to the bread,² other types of leavening agents were sought which would yield relatively tasteless products or actually add flavor to the bread.

There were finally evolved therefore what are now the modern baking powders which consist of dry mixtures of bicarbonate of soda with one or more chemical compounds capable of decomposing the former and releasing the full carbon dioxide content. Usually a filler or drying agent such as starch or flour is also added, the chief functions of which are to prevent premature reaction between the soda and the

¹Thorpe's Dictionary of Applied Chemistry, Vol. 1, p. 664 (1921).

²Davis and Maveety state that sodium bicarbonate added in the proportion of 1.5 lbs. per barrel of flour imparts no unpleasant taste to the bake. See Ind. & Eng. Chem., Vol. 14, p. 210 (1922).

other ingredient and also to aid in the uniform distribution of relatively small quantities of the reacting materials.

The following ingredients mixed with bicarbonate of soda have been employed with more or less success in the manufacture of baking powders:

Tartaric acid and acid tartrates, sodium and potassium acid sulfates, alum and the acid salts of phosphoric acid. In addition to these, limited quantities of carbonate and bicarbonate of ammonia are employed by confectioners in baking certain types of cake and pastries where the character of the finished product is such as to insure the elimination of the ammonia.

Government regulations and the rigid specifications of the trade have made the baking powder industry one requiring both experience and skill. The product must first of all be pure and practically free from anything but the smallest traces of arsenic, lead, zinc, copper and fluorides. The average baking powder must also have such a character or baking strength that when the dough or batter is mixed and baked, carbon dioxide will be evolved at the optimum rate to insure the proper cellular structure of the product.

It is hardly within the scope of the present work to discuss in detail the relative merits of the various baking acids and compounds. Each has its merits and each has been criticized by the manufacturer of the other types in efforts to prove the superior qualities and character of his own particular product.

It must be admitted, however, that the use of acid phosphates as one of the active ingredients of baking powder and self-rising flour has constantly grown in favor until the annual consumption has reached surprising proportions,³ particularly when we consider what relatively small quantities are employed per pound of flour.⁴

The chief reasons for the great popularity of phosphate powders are first their relative low cost to the consumer and second because compounds of phosphorus play an important part in the human diet and therefore when we incorporate small additional quantities in our bread, pastries, etc., we are adding nothing which can be regarded as deleterious to health, but a product which is believed by certain investigators to contribute to the building up of bone and tissue.⁵

* Because of the highly competitive nature of this business the manufacturers are loath to give statistics on their production but the annual consumption is well over twenty-five million pounds.

³ 1.7 lbs. of monocalcium phosphate mixed with 15 lbs. of sodium bicarbonate will leaven 100 lbs. of flour

⁵ Hutchinson, *Food and Dietetics*, Chap. 16 (1900).

There is, however, considerable difference of opinion regarding the nutritive value of inorganic phosphates. Jago⁶ concludes that the balance of evidence is in favor of the view that ordinary diet contains more than a sufficiency of phosphorus and therefore the amount present in bread is of but little or no consequence. Holsti,⁷ on the other hand, regards inorganic phosphates as capable of supplying a large measure of the necessary phosphorus of the human body, and suggests that we require phosphorus in the organic form for building up of brain and nerve tissue and as inorganic salts (phosphates) for the building up of bone tissue.

Four phosphate compounds, whether mixed with sodium bicarbonate alone or with other materials, have been employed for baking purposes, namely: Monocalcium phosphate ($\text{CaH}_2(\text{PO}_4)_2$), Monopotassium phosphate (KH_2PO_4),⁸ Monosodium phosphate (NaH_2PO_4) and Sodium acid pyrophosphate ($\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$).

These compounds when mixed with sodium bicarbonate and a filler or diluent such as flour or cornstarch constitute what are known as straight phosphate baking powders.

With the exception of sodium acid pyrophosphate these phosphates are fast acting baking acids—their reaction with sodium bicarbonate usually beginning promptly in the cold dough, and the final liberation of carbon dioxide being completed in the baking process.

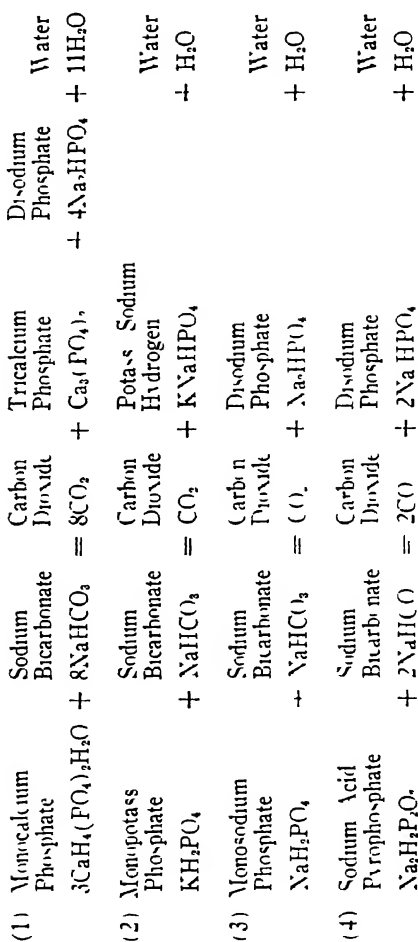
In order to produce slower acting baking powders the acid phosphate may be mixed with calcined sodium aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$) which acts but slightly on sodium bicarbonate in the cold, but reacts readily with this compound at elevated temperatures producing carbon dioxide, sodium sulfate and aluminum hydroxide. Much of the baking powder now on the market carries as its acid ingredients mixtures of monocalcium phosphate and sodium aluminum sulfate.

While there is considerable difference of opinion regarding the reactions taking place between sodium bicarbonate and the four acid phosphate salts mentioned above, these reactions may be stated in their simplest form as follows:

⁶The Technology of Breadmaking, p. 389 (1921).

⁷Loc. cit.

⁸Leavening Agents, p. 52.

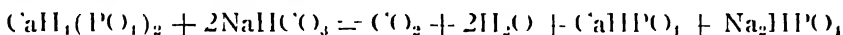


Where a single base is present in a baking powder, as is the case with those containing monosodium and sodium acid pyrophosphate (equations 3 and 4), the chemical reactions involved are fairly simple and probably proceed as outlined in equations 3 and 4, but where two bases are present in a reactive mixture containing a primary phosphate (as is the case with monocalcium phosphate powders), the chemical changes involved are more complex.

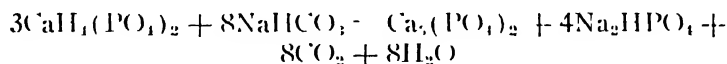
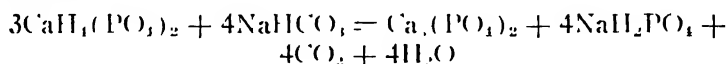
Authorities therefore have held such different views regarding the reactions between monocalcium phosphate and sodium bicarbonate, and the composition of the end product that great confusion prevails on this point.

Hart, for instance, writes the reaction between monocalcium phosphate and sodium bicarbonate as shown in equation (1) above.

Both Leach⁹ and Jago,¹⁰ however, consider that the end of the reaction proceeds no further than dicalcium and disodium phosphate. They write the reaction thus:



Patten¹¹ states that the reaction between monocalcium phosphate and sodium bicarbonate always results in the formation of tricalcium phosphate. Any variation in the proportion of sodium bicarbonate produces a variation in the monosodium and disodium phosphate content of the final product. He expresses these reactions by the two following equations:



Davis and Maveety,¹² after a long series of laboratory experiments, concluded that if a monocalcic powder contains a liberal excess of sodium bicarbonate the resultant products are tricalcium phosphate and disodium phosphate, otherwise a certain amount of dicalcic phosphate will be present.

Neutralizing Strength of Baking Acids.

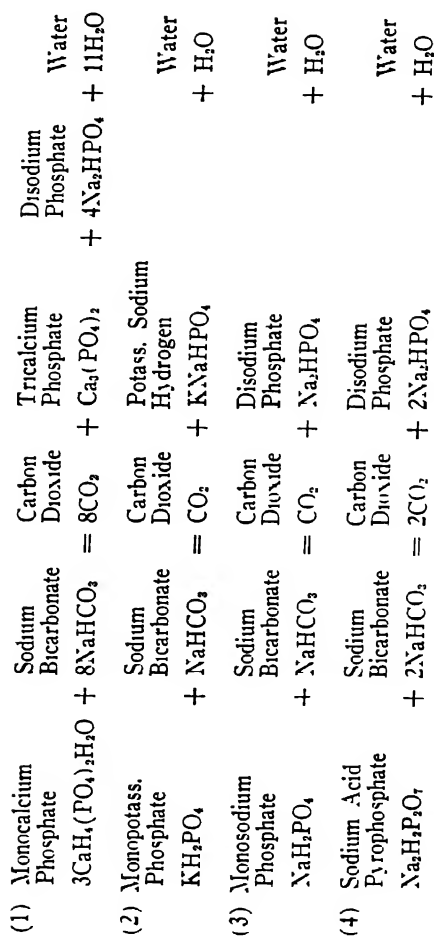
Monocalcium phosphate as well as all other baking acids are largely sold on the basis of their neutralizing strength in terms of sodium carbonate.

⁹ Food Inspection and Analysis, 4th Edition, p. 349.

¹⁰ Technology of Breadmaking, p. 357 (1921).

¹¹ Assoc. of Official Agric. Chemists, Vol. 2, p. 225 (1917).

¹² Jour. Ind. & Eng. Chem., Vol. 14, p. 210 (1922).

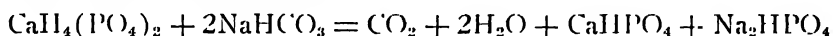


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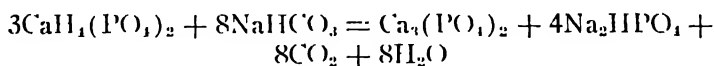
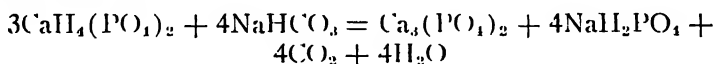
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Hart, for instance, writes the reaction between monocalcium phosphate and sodium bicarbonate as shown in equation (1) above.

Both Leach⁹ and Jago,¹⁰ however, consider that the end of the reaction proceeds no further than dicalcium and disodium phosphate. They write the reaction thus:



Patten¹¹ states that the reaction between monocalcium phosphate and sodium bicarbonate always results in the formation of tricalcium phosphate. Any variation in the proportion of sodium bicarbonate produces a variation in the monosodium and disodium phosphate content of the final product. He expresses these reactions by the two following equations:



Davis and Maveety,¹² after a long series of laboratory experiments, concluded that if a monocalcic powder contains a liberal excess of sodium bicarbonate the resultant products are tricalcium phosphate and disodium phosphate, otherwise a certain amount of dicalcic phosphate will be present.

Neutralizing Strength of Baking Acids.

Monocalcium phosphate as well as all other baking acids are largely sold on the basis of their neutralizing strength in terms of sodium carbonate.

⁹ Food Inspection and Analysis, 4th Edition, p. 349.

¹⁰ Technology of Breadmaking, p. 357 (1921).

¹¹ Assoc. of Official Agric. Chemists, Vol. 2, p. 225 (1917).

¹² Jour. Ind. & Eng. Chem., Vol. 14, p. 210 (1922).

The two general methods employed in determining the neutralizing strength of an acid phosphate are:

- (1) By titration with standard alkali solution.
- (2) By determination of the amount of CO_2 evolved on treating a definite weight of the phosphate with sodium bicarbonate.

It has been clearly demonstrated that the results obtained by titration vary, according to the method employed,¹³ and from what has been brought out by Patten¹⁴ and Davis & Maveety¹⁵ the quantity of CO_2 evolved by a definite weight of monocalcium phosphate is dependent to a considerable extent on the proportion of sodium bicarbonate added. Under these conditions, therefore, it would appear that the valuation of a baking acid may vary considerably depending on the analytical method employed and the experience and skill of the manipulator.

An indirect titration method used by the Victor Chemical Works and recently described by Adler and Barber¹⁶ for determining the neutralizing value of monocalcium phosphate appears to give results which are not only consistent but which are commensurate with those obtained in actual baking tests. The experiments from which this analytical method was developed have confirmed the work of previous investigation in showing that the reaction between monocalcium phosphate and sodium bicarbonate goes beyond the dicalcium stage. While it is not within the scope of this book to present and discuss in detail all of the experimental evidence, the bulk of the work conducted, points strongly to the fact that the end products resulting from the use of monocalcium phosphate baking powders are largely disodium and tricalcium phosphates.

If the reaction goes to an end, therefore, 100 parts of pure monocalcium phosphate will react completely with 88.89 parts of sodium bicarbonate without leaving any residual sodium carbonate. This is the reaction represented in equation (1).

Such a high neutralizing strength, however, is seldom if ever attained with commercial monocalcium phosphate unless free phosphoric acid is present. This free acid affects adversely the physical or mechanical condition of the product, causes the baking powder manufactured therefrom to have poor keeping qualities and upsets its even action in the mixing and baking processes.

Therefore, though the theoretical neutralizing strength of mono-

¹³ Wadman, J. Amer. Chem. Soc., Vol. 16, p. 333 (1894); Bailey, L. H., J. Assoc. Official Agr. Chemists, Vol. 8, pp. 444 and 490 (1925).

¹⁴ Loc. cit.

¹⁵ Loc. cit.

¹⁶ A Study of the Determination of the Neutralizing Value of Monocalcium Phosphate Cereal Chemistry, Vol. II, p. 380 (1925).

calcium phosphate (according to equation (1)) is 88.89, it is seldom desirable to manufacture a product with a neutralizing strength above 80 to 82. Such a product contains as a rule enough dicalcium phosphate to insure the absence of free phosphoric acid with its attendant difficulties in drying and mixing and its probable premature reaction when mixed with sodium bicarbonate.

In the preparation of baking powder from monocalcium phosphate or any other baking acid it is also highly important that little or no excess of sodium bicarbonate is present over that which will be acted upon by the acid salt, since the heat of the oven will decompose this excess, producing normal sodium carbonate which, as previously stated, tends to give a yellow color and unpleasant taste to the baked product.

Composition of Baking Powders and Effects of Residual Salts

The proportions of the ingredients in various brands of baking powder differ considerably, but the United States definition and Standard¹⁷ stipulates that they must yield not less than 12 per cent of available carbon dioxide. The majority of powders are made up so that the finished product will contain from 26 to 29 per cent of sodium bicarbonate and sufficient of the acid ingredients to decompose the bicarbonate and yield from 14 to 15 per cent of carbon dioxide. The balance of the powder consists of cornstarch or some other suitable diluent.

In the following graphic charts (Figures 56, 57), three of which were compiled by Dr. J. R. Chittick and published by the Jaques Manufacturing Company of Chicago, are shown the proportions of the various ingredients employed in several types of baking powder and the composition and quantities of the products resulting from the chemical reactions involved.

Since Dr. Chittick did not include a chart on a baking powder containing sodium acid pyrophosphate the fourth figure was drawn up by the writers along the same lines as the first three.

All of the baking powders in the above figures are so proportioned that they will yield (theoretically) 14 per cent of carbondioxide, and while the weights of the acid ingredients and diluent vary, the actual weight of the sodium bicarbonate is the same in every instance. Of the straight phosphate powders, that made up with monocalcium phosphate requires the least, and that containing sodium acid pyrophosphate requires the greatest quantity of acid ingredient, but this latter acid has certain desirable properties which make it particularly suitable for certain baking purposes.

¹⁷ Food Inspection Decision No. 174, issued Feb. 26, 1918.

The effect of the inorganic salts resulting from the interaction of sodium bicarbonate and the various baking acids on the properties of bread was the object of an investigation conducted by Smith and Bailey.¹⁸

This investigation included the four following lines of research:

- (1) A study of the effect of these residual salts when mixed with

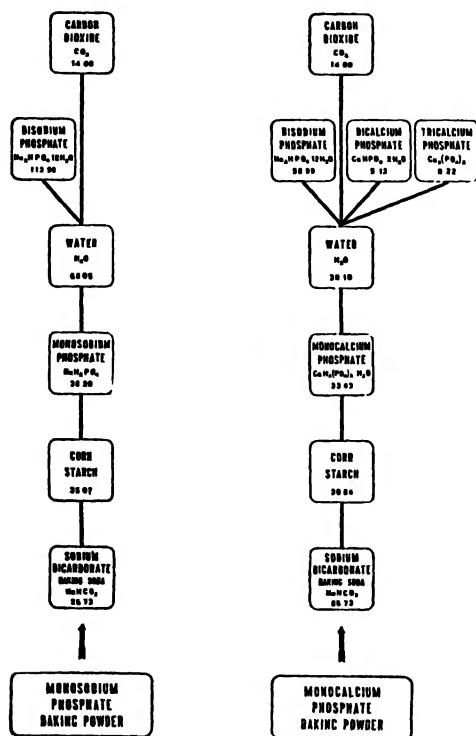


FIG. 56.—Diagrams Representing Reactions Taking Place in Oven When Monosodium Phosphate and Monocalcium Phosphate Baking Powders Are Used.

flour to form a dough and the glutens washed, (2) The washing out of the gluten content of flour and then immersing it in the salt solution for 24 hours, (3) Determination of the hydrogen ion concentration of doughs and biscuit prepared with baking powders or residual salts, (4) Testing doughs so treated to determine their elasticity and extensibility.

¹⁸ The Effect of Chemical Leavening Agents on the Properties of Bread, Jour. Amer. A. soc. of Cereal Chemists, Oct. (1923).

It was observed that of all the residual salts resulting from the interaction of sodium bicarbonate and the baking acids, disodium phosphate has the greatest effect on the gluten content of bread, tending to keep it from forming a tough, firm compact mass. In discussing the effect of this salt the writers state:

"A certain measure of hydration of the gluten, such as is observed

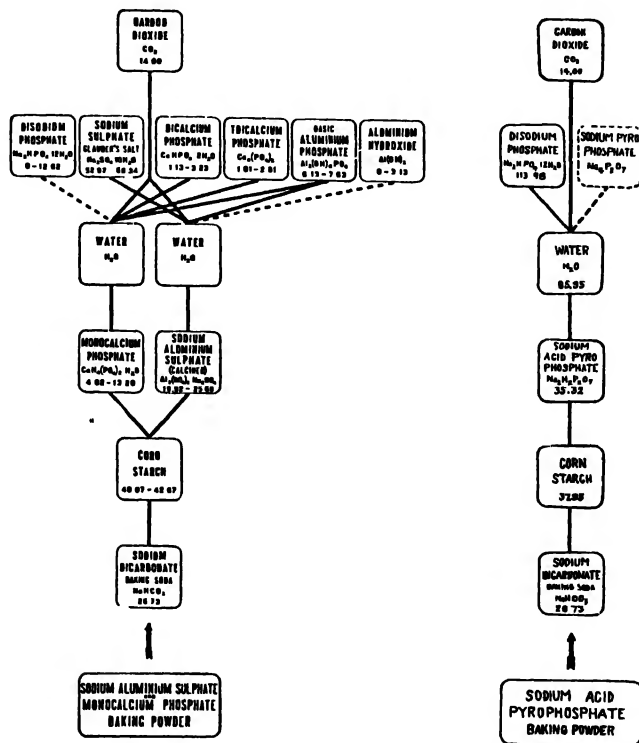


FIG. 57.—Diagrams Representing Reactions Taking Place in Oven with Phosphate and Alum Baking Powder and with a Powder Containing Sodium Acid Pyrophosphate as its Acid Ingredient.

in the use of this salt, may be advantageous in imparting a degree of friability and shortness to biscuit. In view, however, of the large proportion of the salt which results from the use of monosodium phosphate powder with a 14 per cent gas strength, the concentration of the residual salt may be too great."

This statement is interesting when considered in connection with powders containing sodium acid pyrophosphate. It is a disputed question whether the residual salt resulting from the interaction of sodium

acid pyrophosphate and sodium bicarbonate is normal sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) or disodium phosphate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$). The fact that biscuit baked with this acid are plumper may be an indication that a portion of the residual salt is in the form of sodium pyrophosphate which probably has less effect on the gluten content and the elasticity of the dough.

Manufacture of Monocalcium Phosphate.

The manufacture of monocalcium phosphate for baking powder purposes would appear offhand to be a relatively simple procedure, but there are a number of details in the process which have been learned only by long and costly experience, and a knowledge or lack of knowledge of these details may well mean the difference between profit and loss. Moreover, the high standards set by the state and Federal Food and Drug acts are such that only the purest of raw materials can be used in making the final product and the greatest care must be taken that no objectionable impurity or foreign matter is introduced during the processing or manipulation of these raw materials. So keen has the competition become in this industry that even the slightest discoloration of the product may seriously militate against its sale.

The procedure employed in manufacturing monocalcium phosphate differs considerably in detail depending on the type of raw material employed and the quality and strength of the phosphoric acid.

Meckstroth¹⁹ gives the following description of the manufacture of monocalcium phosphate:

"The phosphoric acid now ready for the production of the acid salt is weighed and added slowly, under continual agitation to a weighed amount of the alkali or neutral salt²⁰ and thoroughly mixed. As the reaction requires considerable time for completion, it is advisable to add a slight excess of acid and then give ample time for the reaction to go to completion and all the free acid to disappear. At least 24 to 48 hours should be allowed for this ageing process to take place. After proper ageing, the acid salt is dried at a temperature of approximately 85° C., preferably in a rotary or shelf vacuum dryer, until a product containing not over one per cent of moisture is obtained. A higher moisture content is detrimental both to the grinding or milling process and in the baking chemicals in which it is to be used.

"The grinding of the acid salt is not a difficult operation. Under unfavorable weather conditions, considerable caking takes place, espe-

¹⁹ Manufacture of Phosphoric Acid and Phosphates, Chem. & Met. Eng., Vol. 26, No. 2, p. 79 (1922).

²⁰ By neutral salt Meckstroth apparently means dicalcium phosphate.

cially in damp climates. The grinding is followed by the screening operation, in which the powdered and granular portions are classified.

"After the acid salt is properly granulated or powdered, it may be standardized to any strength desired by the addition of a neutral or inert substance, such as dicalcium phosphate or calcium sulfate. The calcium sulfate cannot be classed as an inert substance and the present tendency is to eliminate the so-called sulfate phosphate from the baking industry. The leading phosphate manufacturers are taking the initiative and advising their customers to use only the full strength or the higher test phosphate."

While it may be true that in manufacturing monocalcium phosphate from pure dicalcium phosphate the time factor is an important one, the writers feel that Meckstroth has laid undue stress on this point. It is certainly true that where certain calcium compounds and fairly concentrated phosphoric acid are employed the reaction takes place with great rapidity and is practically complete within a comparatively short period of time, provided of course, that care is taken to thoroughly mix the reacting ingredients.

The following description of the manufacture of monocalcium phosphate is perhaps more nearly typical of the average modern practice.

A batch of 500 pounds or more of hydrated lime or some other form of calcium is dumped into a mechanical mixing pan and sufficient phosphoric acid (50 to 55° B \acute{e} .) is added to convert practically all of the lime into monocalcium phosphate. While it is desirable to obtain an acid salt with as high a neutralizing strength as possible, care must be taken that no free phosphoric acid is present in the final product, as this will not only make it more difficult to dry but increase its tendency to deteriorate when mixed with sodium bicarbonate.

The reaction which takes place is both energetic and rapid and large quantities of water are evolved in the form of vapor.

The stirring is continued until the mass sets up. The material is then removed from the mixer and usually spread upon a floor for further drying and to insure the completion of the reaction. This curing takes from 12 to 18 hours longer.

The lumps of acid phosphate, not larger than a hickory nut, are in turn fed to a steam heated vacuum dryer where all but about one per cent of free moisture is driven off. The drying process must be very carefully conducted since overheating will cause reversion of the mono and a loss in its neutralizing strength.

After drying, the material is milled and separated into various grades (according to fineness) by means of shaker or vibrating screens.

Baking powders made from mixtures of extremely finely ground monocalcium phosphate and powdered or precipitated sodium bicar-

bonate do not keep so well even when moderately diluted with starch or flour. These very fine powders are termed baking creams and find their chief use in self-rising flour where they are uniformly distributed through such a mass of the diluent that they do not deteriorate before using. The use of self-rising flours containing acid phosphate has grown to large proportions particularly in the Southern States where hot biscuits are so universally consumed.

High grade monocalcium phosphate for baking purposes should have the following average composition:

Free phosphoric acid (H_3PO_4)	= None
Monocalcium phosphate ($CaH_2(PO_3)_2 \cdot H_2O$)	= 85.5 to 90.0
Dicalcium phosphate ($CaHPO_4 \cdot 2H_2O$)	7.5 to 8.0
Calcium sulfate	0.5 to 1.0
Iron and aluminum phosphates	1.0 to 1.5
Moisture and insoluble	1.0 to 1.5
Arsenic and lead (under Gov't. allowance)	

In a recent patent issued to Wm. E. Stokes²¹ the inventor claims a method of producing high strength monocalcium phosphate free from dicalcium phosphate and free phosphoric acid. Briefly the process consists in first passing the monocalcium phosphate (containing free H_3PO_4) through a vacuum drier and then mixing it with one-half as much calcium carbonate as there is free phosphoric acid present.

Straight phosphate baking powders are usually made up of granular²² materials to prevent premature reaction between the two main ingredients. Where monocalcium phosphate is mixed with sodium aluminum sulfate it is not so important to have the phosphate in granular form and therefore such baking powders contain more finely divided material.

The annual production of monocalcium phosphate for baking powder purposes is estimated at not less than 60,000,000 lbs. or 30,000 short tons.

Manufacture of Monosodium Phosphate and Sodium Acid Pyrophosphate.

Monosodium phosphate is manufactured in a manner similar to that employed in producing monocalcium phosphate. For example, sodium carbonate or some other compound of soda and phosphoric acid are thoroughly mixed and the product dried directly or crystallized.

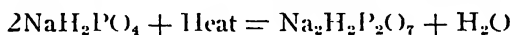
²¹ U. S. Patent No. 1,538,910 (1925).

²² Granular monocalcium phosphate is so prepared that all but a trace will pass through an 80-mesh screen, but the bulk of it will be retained by a 200-mesh screen.

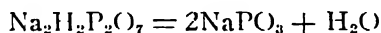
Monosodium phosphate, however, is not an altogether satisfactory baking acid due to its hygroscopicity and hence its poor keeping qualities when mixed with sodium bicarbonate unless sealed in airtight containers and used within a relatively short time after the package has been opened.

Sodium acid pyrophosphate, however, keeps far better than the acid salt of orthophosphoric acid, being nonhygroscopic and less energetic in its action on sodium bicarbonate. It is what may be termed an even baking acid, reacting but slowly in the cold dough and thus reserving the greater portion of its leavening power to be exerted during the actual baking process.

This baking acid is manufactured by heating monosodium phosphate to a temperature ranging between 225° and 250° C. for a period of from 6 to 12 hours, when the following reaction takes place:



If heated above 250° C. sodium acid pyrophosphate loses a further quantity of water and is converted in part to sodium metaphosphate, thus:



This latter compound has no acid properties and is of little or no commercial value. It is highly essential, therefore, that the temperature to which monosodium phosphate is heated in order to produce the acid pyrophosphate be very closely controlled.

Chapter 9.

"The Use of Phosphates as Water Softeners and the Manufacture of Trisodium Phosphate."

Practically all natural waters contain to a greater or less extent impurities in suspension or in solution which lessen their value for certain industrial uses such as boiler feed water, city supplies of potable water, in laundering and for the textile and various other chemical industries. It is often necessary, therefore, to remove or alter the composition of these detrimental impurities before such waters can be economically utilized. The property which certain dissolved salts impart to water is termed "hardness" and the methods of removing this property are generally known as water softening processes.

The suspended material can usually be removed by simple filtration processes and so will not be further discussed, but the removal of the impurities in solution presents a more complex and difficult problem. The most common of these impurities¹ are, magnesium sulfate, calcium sulfate, calcium and magnesium bicarbonates, calcium and magnesium chlorides, calcium and magnesium nitrates, sulfates of iron and aluminum, and various alkali metal salts. In recent years the phosphates of soda—disodium and trisodium phosphate (particularly the latter) have assumed great prominence as water softening compounds.

"The Softening of Boiler Feed Waters."

The most important problem from an economic standpoint is that of treating waters for use in steam boilers. Since in the production of steam only the volatile portions of the feed water is utilized, any salts which enter the boiler as soluble impurities are left behind, and there is gradually formed a sediment crust or scale in the tubes which reduces the efficiency of the boiler.

These scales are of two general types: the "soft" or carbonate scales and the "hard" or sulfate scales. Owing to the density and mechanical structure of these deposits they form excellent insulators² which pre-

¹ The Purification of Boiler Feed Water, E. Brown, Chem. and Met. Eng., 13, pp 156-60 (1915).

² Fiske, E. W., Univ. of Texas, Bull. No. 1752, p. 29 (1917), states that where the rate of evaporation is high, the body of the scale is dry or contains only

vent efficient heat transfer from the fuel to the boiler water. Prof. Schmidt³ of the University of Illinois in the following table (Table LVI) gives results showing the decrease in heat transfer efficiency of tubes coated with scales of different thicknesses and composition.

TABLE LVI
LOSS OF EFFICIENCY IN HEAT TRANSFER THROUGH BOILER SCALES OF DIFFERENT THICKNESS AND COMPOSITION

Character of Scale	Thickness	Composition	Loss of Efficiency
	Inch		Per Cent
Hard	$\frac{1}{60}$	Mostly carbonate	9
Soft	$\frac{1}{32}$	" "	7
Hard	$\frac{1}{32}$	" "	8
Soft	$\frac{1}{25}$	" "	8
Hard	$\frac{1}{25}$	Mostly sulphate	9
"	$\frac{1}{20}$	" "	11
Soft	$\frac{1}{16}$	" "	10
"	$\frac{1}{16}$	Mostly carbonate	11
"	$\frac{1}{16}$	" "	12
Hard	$\frac{1}{16}$	" "	12
Soft	$\frac{1}{11}$	" "	15
Hard	$\frac{1}{8}$	Mostly sulphate	16

Thus it can be seen that a great saving in fuel may be effected by the use of waters without scale forming properties.

Calcium and magnesium carbonates present in the water as bicarbonates usually form a soft scale which is not difficult to remove, but when present as sulfates or mixtures of sulfates and carbonates the scale is hard (like a cemented mass) and clings tightly to the tube walls.

The Use of Boiler Compounds.

There are two general methods employed in softening water for boiler use, namely: that in which the scale forming compounds are removed before the water goes to the boiler, and that in which the water is softened after entering the boilers. The most suitable method to employ is dependent on the size and type of plant and on the composition of the water as well as that of the boiler compound.

There are many types of boiler compounds in use at the present time. While most of these have as a base sodium carbonate or hydrate, the phosphates of soda play an important rôle in certain water softening preparations, not only because of their property of preventing scale, superheated dry steam, which condition approaches that of a dry pipe covering and thus forms an excellent heat insulator.

³ Boiler Water Treatment, Bur. of Mines Tech. Paper No. 218 (1919).

but also on account of their mechanical effect. Di- and trisodium phosphates probably react with the salts of calcium, magnesium and iron to form insoluble phosphates according to the following reactions:

- (1) $3\text{CaCO}_3 + 2\text{Na}_3\text{PO}_4 = \text{Ca}_3(\text{PO}_4)_2 + 3\text{Na}_2\text{CO}_3$
- (2) $3\text{MgSO}_4 + 2\text{Na}_3\text{PO}_4 = \text{Mg}_3(\text{PO}_4)_2 + 3\text{Na}_2\text{SO}_4$
- (3) $\text{FeCl}_3 + \text{Na}_3\text{PO}_4 = \text{FePO}_4 + 3\text{NaCl}$
- (4) $3\text{CaH}_2(\text{CO}_3)_2 + 2\text{Na}_3\text{PO}_4 = \text{Ca}_3(\text{PO}_4)_2 + 6\text{NaHCO}_3^4$
- (5) $\text{CaH}_2(\text{CO}_3)_2 + \text{Na}_2\text{HPO}_4 = \text{CaHPO}_4 + 2\text{NaHCO}_3^4$
- (6) $\text{CaSO}_4 + \text{Na}_2\text{HPO}_4 = \text{CaHPO}_4 + \text{Na}_2\text{SO}_4$

The above phosphate precipitates are in a flocculent condition and do not settle out while the water is in a state of ebullition. Their concentration, however, increases as the water evaporates to form steam and new supplies of water are added to the boiler, so that it is necessary to remove this precipitate from time to time. This is accomplished while steaming by "blowing off" at the surface of the water in the boiler, and by a bottom "blow off" if the water in the boiler is quiet. Whenever practicable the sodium phosphates should be added and the precipitates removed before the water enters the boiler, as this saves considerable trouble and prevents the waste of steam entailed in "blowing off" at frequent intervals.

In addition to their chemical effect phosphates of soda in water softening compounds are said to reduce the objectionable property of foaming caused by the presence of soluble salts in boiler waters. Tri- and disodium phosphates are used in a large number of the patented ^a boiler compounds.

Elberbach ^b proposes the use of a compound containing trisodium phosphate (75 per cent) sulfate of ammonia (8 per cent) and soda ash (17 per cent). He states that in the presence of sodium carbonate the ammonium sulfate is rendered active and imparts to the phosphates a peculiar affinity for the lime and magnesia in solution, causing them to precipitate. Payne ^c suggests the use of a solution of trisodium phosphate with an excess of caustic soda, the latter compound being added in an amount only sufficient to precipitate the carbonates in the water while the trisodium phosphate removes the permanent hardness by precipitating the sulfates and chlorides of magnesium and calcium.

⁴ In reactions (4) and (5) the sodium bicarbonate (NaHCO_3) formed, readily breaks down on boiling into sodium carbonate (Na_2CO_3), water and carbon dioxide (CO_2), the carbon dioxide passing off with the steam.

^a A number of the more important U. S. Patents U. S. Patents 1,001,935 (1911); 1,002,603 (1911); 1,078,655 (1913); 1,109,849 (1914); 1,162,024 (1915); 1,181,562 (1916); 1,247,833 (1917); 1,273,857 (1918); 1,278,435 (1918); 1,333,393 (1920).

^b U. S. Patent 1,001,935 (1911).

^c U. S. Patent 1,002,603 (1911).

Ley⁸ and de Brum⁹ employ phosphate of soda as a reagent in preparing a water softener consisting of a complex alkali silicate. Buchner¹⁰ precipitates the soluble calcium and magnesium salts of hard water with disodium phosphate. The precipitation is said to be accelerated by the addition of borax and sodium or calcium carbonate. It is claimed that colloidal calcium and magnesium phosphates are first formed and that these are then precipitated by the borates and carbonates which are included in the softening compound. Barnes¹¹ produces a boiler compound in a slowly soluble cake from 15 parts sodium amalgam, 10 parts tannin, 10 parts kerosene (with the addition of sufficient whale oil or seal oil to emulsify the kerosene), 15 parts of sodium hydroxide, 25 parts of dextrin, 15 parts of trisodium phosphate, and 10 parts of water. The trisodium phosphate is added for the purpose of neutralizing the corrosive action of the feed waters.

Heller¹² proposes to soften hard water for boiler use by treating it with disodium phosphate at a boiling temperature. He claims an advantage is gained by first boiling the water to remove a large part of the temporary hardness and then adding the phosphate.

Campbell¹³ mixes 16 parts sodium carbonate, 3 parts lime, 3 parts sodium silicate, 4 parts caustic soda, 4 parts sodium bichromate, and 2 parts of trisodium phosphate, and presses into a hard brick or into perforated tin cylinders. These bricks or cylinders he suspends in the boiler, and the slow solution of this material causes an even distribution of the softening agent throughout the boiler.

Edser and Tucker¹⁴ propose to precipitate the soluble salts which cause hardness with di- or trisodium phosphate and then adding a soluble soap and agitating to cause a froth which will hold the precipitated salts in suspension. This froth may be removed by overflow or otherwise.

One of the chemical preparations which is said to be quite successful is that known as the "Navy Standard Boiler Compound,"¹⁵ which was developed by F. Lyon, Lieutenant Commander, U. S. Navy. This product consists of a mixture of 76 per cent anhydrous sodium carbonate (Na_2CO_3), 10 per cent trisodium phosphate (Na_3PO_4 — $12\text{H}_2\text{O}$), 1 per cent dextrin or starch, sufficient cutch¹⁶ to yield at least

⁸ U. S. Patent 1,109,849 (1914).

⁹ Ger. Patent 274,650 (1912).

¹⁰ U. S. Patent 1,162,024 (1915).

¹¹ U. S. Patent 1,181,562 (1916).

¹² U. S. Patents 1,247,833 (1917) and 1,273,857 (1918).

¹³ U. S. Patent 1,278,435 (1918).

¹⁴ U. S. Patent 1,333,393 (1920).

¹⁵ A Novel Method of Handling Boilers to Prevent Corrosion and Scale. A. H. Babcock, J. Am. Soc. Mech. Engrs., **38**, pp. 529-38 (1916).

¹⁶ A substance obtained from the bark of mangrove trees.

2 per cent of tannic acid, and water to make up to 100 per cent. The sodium carbonate takes care of any chemical reactions, and gives an alkaline solution which is noncorrosive. The tannic acid and starch by holding the impurities in suspension in a colloidal state prevent the formation of scale. Babcock¹⁷ states that one of the functions of the trisodium phosphate is to prevent the increase in surface tension of the boiler water, and the consequent "priming"¹⁸ caused by the concentration of the impurities and by the addition of the other ingredients in the compound.¹⁹

In order to test the efficiency of this product it was tried out at one of the power plants in California, where it was added to the water used in twelve 645 horsepower water tube boilers. Babcock²⁰ states that the cost of this treatment was only \$80.00 per month and during the first 2 months the number of boiler tubes replaced was decreased from 171 per month to zero and the expense for labor and material reduced from \$10,000 to \$1,200 per annum.

The Softening of Laundry Waters.

Large quantities of water are daily used in the laundries of this country, and while the impurities are often the same as found in boiler feed waters, the removal is for an entirely different purpose. In boilers the conservation of heat is of prime importance, whereas in the laundries the saving of soap and prevention of stains in the cloth are the main objects sought. The most plentiful and objectionable of the salts present in hard waters are lime and magnesium compounds which react with the cleansing reagents to form precipitates ("curds") which deposit on the cloth, shortening its life and causing streaks and stains. Iron and manganese compounds also produce stains which are difficult to remove. It is desirable, therefore, to remove those salts which form precipitates before the addition of the soap and one of the compounds which has been found useful for this purpose is trisodium phosphate. The saving in soap which may be effected by reducing the "hardness" of the water is shown in the following table.²¹

In addition to an average saving of 66 per cent in the soap consumed, the use of these softened waters resulted in a reduction of 74 per cent of the soda and 36 per cent of the water ordinarily required.

¹⁷ Idem.

¹⁸ The ejection of water from the boiler along with the steam

¹⁹ It is stated by S. T. Powell that a concentration of 200 to 300 grains of sodium sulphate per gallon will unquestionably cause priming. (S. T. Powell, *Purification of Waters for Industrial Use*, J. Am Water Works Asso., 10, p. 28 (1923))

²⁰ Loc. cit.

²¹ Powell, S. T., *Purification of Water for Industrial Use*, J. Am Water Works Assoc., 10, p. 31 (1923).

TABLE LVII

SAVING OF SOAP EFFECTED BY LAUNDRIES USING SOFTENING PROCESSES

Name and Location of Laundry	Hardness	Quantity of Soap Used (Lbs.)		Saving of Soap
		Without Softening	After Softening	
	Grains per Gal.			Per Cent
Snow White Laundry, Wilmington, Del.	3½	400	150	62
City Star Laundry, Harrisburg, Pa....	5	772	318	59
American Laundry, Grand Rapids, Mich.	7	973	350	64
Walker's Laundry, Niagara Falls, N. Y.	7	400	96	76
Yale Laundry, Washington, D. C.....	7	621	255	59
Kennedy Laundry, Chicago, Ill.....	8	1,872	671	64
Olean Palace Laundry, Olean, N. Y....	9	170	48	72
Westminster Laundry, St. Louis, Mo....	9	750	250	66
Cascade Laundry, Great Falls, Mon....	10	580	153	73
Imperial Laundry, Albuquerque, N. M...	10	800	132	83
Crown Laundry, Indianapolis, Ind.....	19	954	502	47
Perfection Laundry, Springfield, O....	20	682	224	67
Average.....				66

Waters used in the textile and paper industries must meet very much the same requirements as those used for laundering purposes.

In the tanning industry the water must be fairly free from salts of calcium and magnesium, since these compounds precipitate large quantities of the dyestuffs, oils, waxes and fats present in the tanning material.

Various methods of softening water used in other chemical industries are practiced, depending upon the nature and composition of products sought.

The Use of Phosphoric Acid in Softening Potable Waters.

Phosphoric acid has been employed on a large scale at the Columbus softening and purification works²² in order to produce a fully carbonated water and remove any residual causticity caused by the use of the lime-softening process.

The treatment of carbonated waters with lime cause the precipitation of the bulk of the carbonates, but water so softened carries certain quantities of these relatively insoluble carbonates in suspension or in colloidal solution. The subsequent deposition of these normal carbonates as incrustations on the sand grains of the filters causes a

²² Hoover, C. P., The Use of Phosphoric Acid in Water Softening, Eng. News Record, 86, p. 81 (1921).

material reduction in the efficiency of the filter beds. In order to prevent the formation of such incrustations it was deemed necessary to use some other method of treatment after the water had been softened with lime.

By adding phosphoric acid at the rate of 0.7 grains per gallon of softened water any excess alkalinity is removed, one-half of the normal carbonates present are converted into insoluble phosphates, and the liberated carbon dioxide combines with the remaining carbonates to produce bicarbonates. Thus the residual hardness of the lime softened water is materially reduced and the efficiency of the sand in the filter bed is maintained.

Phosphoric acid or acid phosphate may also be used to treat sewage sludge,²⁴ decomposing the soaps and carbonates present, or causing a flocculent precipitate of dicalcium phosphate which coagulates and carries down the solid or suspended matter, much of which contains nitrogen. The settled residue may be dried and used as a fertilizer material. However, very little has actually been done in a commercial way along this line.

"The Manufacture of Trisodium Phosphate."

Trisodium phosphate is by far the most important compound or phosphoric acid used as a water softener and detergent. In recent years its consumption has grown to large proportions since it possesses a number of physical and chemical properties which make it particularly well adapted to laundry and household use.

This compound as manufactured in a commercial way is a dry crystalline product easy to handle and ship, has a low causticity, is readily soluble in both hot and cold water and is very efficient in throwing out of solution salts of lime, magnesium, iron and aluminum.

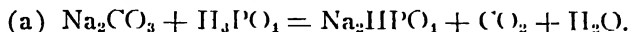
The manufacture of trisodium phosphate is now conducted on an extensive scale and though the reactions involved are relatively simple, experience and skill are required in order to obtain a product which will meet satisfactorily the specifications required by the trade. Moreover, since this business has become a highly competitive one and the producer must work on a rather narrow margin of profit, it is necessary to use the best and most up-to-date mechanical equipment in order to reduce the labor and handling charges to a minimum.

Since the third atom of hydrogen in phosphoric acid cannot be replaced by the sodium in soda ash, the chemical reactions involved in

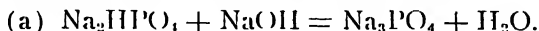
²⁴ McMurtrie, W., Disposal of Sewage with Recovery of Elements of Plant Food for Use in Agriculture, *J. Ind. Eng. Chem.*, **5**, 156-9 (1913); T. K. Irwin, British Patent 13,235 (1914); J. W. Phillips, U. S. Patents 1,284,441 and 1,284,442 (1918).

the manufacture of trisodium phosphate must be carried out in two stages.

(1) The production of disodium phosphate by the action of phosphoric acid on a solution of soda ash thus:



(2) The production of trisodium phosphate by treating the solution of disodium phosphate with sodium hydroxide thus:



The process is carried out in a general way as follows:

The solution of soda ash (along with the mother liquor from a previous batch of trisodium phosphate) is run into large steel lined tanks fitted with mechanical stirrers and having steam coils to keep the solution at boiling temperature. Sufficient strong phosphoric acid is then added to produce a solution of disodium phosphate which is pumped to a filter press to remove certain precipitated impurities. The cake in the filter press is then washed and the wash water used to help dissolve the next batch of soda ash.

The clear solution of disodium phosphate is then pumped into another mixing vat similar to those employed in the first step and a sufficient quantity of a strong solution of caustic soda added to produce a saturated solution of trisodium phosphate. This hot solution is also passed through a filter press and is then either run into crystallizing tanks or through a mechanical crystallizer where it is cooled. During the cooling operation most of the trisodium phosphate drops out in the form of needlelike crystals containing 12 molecules of water of crystallization ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$).

These crystals are drained and then shoveled into a centrifuge, washed, with a small quantity of water to remove the mother liquor and whirled till they contain less than 10 per cent of free moisture. They are then discharged into a hopper and fed to a rotary drier and dried at a temperature insufficient to drive off the water of crystallization.²⁴

The product is then cooled to prevent subsequent caking, discharged into the boot of an elevator and either carried to a storage bin or run over screens to separate the fines from the coarse crystals. The one or more grades of crystals are then packed in barrels, kegs, or sacks for the market.

The mother liquor from the drained crystals as well as that from the wringer goes back into the system in making up new charges. The cycle being repeated until this liquor is too impure for use.

²⁴ Since $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ dissolves in its own water of crystallization at 70 degrees C. great care must be exercised in drying the product.

A flow sheet showing the main steps in the manufacture of trisodium phosphate is given in Figure 58.

A recent patent issued to L. D. Mathias²⁵ describes methods of manufacturing a product which can be used as a combined germicide and cleansing agent. The material seems to offer considerable promise, and should meet a need where both an antiseptic and detergent are now required.

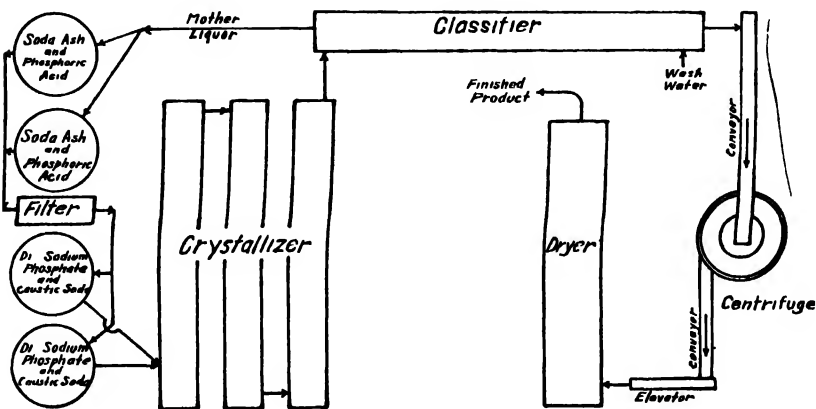


FIG 58—Trisodium Phosphate Flow Sheet

According to the inventor, this product which has most of the properties of trisodium phosphate, but contains in addition from 1 to 3 per cent of available chlorine may be manufactured in a number of ways: (1) By adding sodium hydroxide and sodium hypochlorite to a saturated solution of disodium phosphate. (2) By adding to a saturated solution of trisodium phosphate, from 2 to 10 per cent of sodium hydroxide and then passing chlorine gas slowly into the solution while maintaining the temperature at 50° C.

Since only from two-thirds to three-fourths of this compound crystallizes out on cooling the solution, the mother liquor may again be brought up to the desired composition by the addition of sodium phosphate, sodium hydroxide, and sodium hypochlorite or chlorine gas.

The final product is a colorless crystalline mass, which if properly prepared can be dried and kept for a long period of time with little or no loss of its chlorine content.

No accurate figures are available showing the production of trisodium phosphate, but a conservative estimate of the annual output is 40,000,000 lbs. or 20,000 short tons.

²⁵ U. S. Patent No. 1,555,474 (1925).

Chapter 10.

Miscellaneous Uses of Phosphoric Acid.

"PHOSPHORIC ACID AS A RUST PROOFING AGENT."

The prevention of the corrosion of iron and steel surfaces exposed to abnormal or even ordinary oxidizing conditions is a problem on which much time and careful research has been spent. The importance of having rust proof coatings which penetrate or molecularly bond themselves to metal surfaces and hence are not subject to deterioration from contraction and expansion was early recognized, and a number of processes based on the formation of oxide, sulfide or metallic films have been tried with more or less success. Many of these processes, however are either so costly or uncertain¹ that they cannot be successfully employed for general use and therefore the development of the phosphate or "Parker Process" has been a real boon to the manufacturer of steel products.

Principle on Which Phosphoric Acid Rust Proofing is Based.

The use of phosphoric acid as a rust proofing agent was proposed by Coslett in 1907, and this process (while later modified and considerably improved) contains the fundamental principle on which the more up-to-date methods are based.

The original Coslett process was based on the fact that phosphoric acid solutions will dissolve ferrous phosphate within certain definite limits in direct proportion to the concentration of the acid present. The addition of any metal base such as iron or steel which is capable of entering into combination with the free acid present in such solutions (which are already practically saturated with iron phosphate) results in the precipitation of ferrous phosphate on the metal surface at the point of solution. The reaction takes place with the evolution of hydrogen until the metal surface is coated with a basic iron phosphate.

As developed on a commercial scale, Coslett's process consisted in mixing iron filings with concentrated phosphoric acid until a thin paste of ferrous phosphate was obtained. This paste was then added to weak

¹ Whittier, E. S., *Black Finishes on Iron and Steel*, Metal Industry, Vol. 16, p. 509 (1918).

boiling phosphoric acid and the iron or steel articles on which it was desired to deposit the rust proof coating were immersed in this solution for three or four hours. They were then removed, cleaned, dried and oiled.

Unfortunately considerable difficulty was encountered in obtaining uniform coatings by this process. Much of the salt suspended in the solution adhered loosely to the metal and in some instances incorporated itself with the rust proof coating, increasing the dimensions of the articles, which in the case of machined work is very objectionable.

It was therefore necessary to modify this process to take care of these troublesome features.

Development of the Parker Process.

According to Eckelmann,² Messrs. Allen and Richards were mainly responsible for modifying this process so as to render it one of the simplest and cheapest rust proofing methods known. Their patented modification as now practiced is known as "Parkerizing."³

The Parker method was gradually developed from a number of patented processes invented by Richards and Allen. Most of these processes include the use of an oxidizing agent.

The first of these patents issued to Richards,⁴ in 1913, consists of a rust proofing solution containing the following ingredients:

Concentrated phosphoric acid	0.5 gallon
Manganese dioxide	3.0 pounds
Water	120.0 gallons

It is claimed that by heating this solution to the boiling point and immersing iron or steel articles therein, a rust proof coating is formed over the metal surfaces.

In another patent issued to Allen⁵ in 1917, the inventor claims that rust proof coatings may be formed on iron and steel articles by exposing them for one or two hours to fumes of P_2O_5 containing water vapor. The metal articles being constantly tumbled or moved about

²Phosphatic Coatings for Rust Proofing Iron and Steel, Chem. and Met. Eng., Vol. 21, p. 787 (1919).

³Morrow, L. C., Parkerizing, A Rust Proofing Process, American Machinist, Vol. 57, pp. 361-364 (1922); Parker Rust Proofing Process, Chem. and Met. Eng., Vol. 18, pp. 264-7 (1918); Eckelmann, Parkerizing, a Combined Rust Proofing and Finishing Process, Raw Materials, Vol. 5, pp. 438-9 (1922); Whittier, E. S., Black Finishes on Iron and Steel, Metal Ind., Vol. 16, p. 509 (1918); Whittier, E. S., Rust Proofing of Iron and Steel, Met. Ind., Vol. 17, p. 79 (1919).

⁴U. S. Patent 1,069,903 (1913).

⁵U. S. Patent 1,248,053 (1917).

to insure that the acid vapors come into contact with all parts of the metal surfaces.

In a later patent, Allen ⁶ describes a rust proofing stock solution consisting of phosphoric acid and sodium dichromate mixed with water in the following proportions:

Phosphoric acid (75 per cent)	=	66.60	pounds
Sodium dichromate	=	0.78	"
Water	=	100.00	"

This stock solution is diluted with water (till 100 cc. neutralize 150 cc. of N/10 potassium hydroxide) heated to the boiling point, and the iron or steel articles immersed therein for a period of two hours. Potassium or sodium permanganate may be substituted for sodium dichromate if desired.

By adding a small quantity of zinc, either as the metal, oxide, or phosphate, to a bath containing phosphoric acid and an oxidizing agent, Allen ⁷ claims that a darker and more resistant rust proof coating is formed on iron and steel than in baths free from zinc compounds. The proportions of zinc and manganese dioxide employed may be varied between rather wide limits, but the preferred proportions made up into a very dilute solution are as follows:

Phosphoric acid	50	parts
Manganese dioxide	14	"
Zinc	0.14 to 1.4	parts

In the final development of the "Parker Process" or "Parkerizing" as practised to-day, the old Coslett solution as described on page 279 is altered by adding an oxidizing agent such as manganese dioxide to a 0.75 per cent solution of phosphoric acid containing ferrous phosphate. This latter salt is thus partially oxidized to the ferric condition by continual agitation and boiling. The correct ratio between the ferrous and ferric salts being 3 of the former to 1 of the latter. Morrow ⁸ states that the rust proofing solution contains a total of only 1 per cent of iron, manganese and phosphoric acid.

The coating formed on the metal surfaces by such a solution is a basic ferrous—ferric phosphate of somewhat indefinite composition, but the principle of its deposition is the same as in the original Coslett process. During the oxidation process some manganese phosphate is formed, which it is said also possesses rust proofing properties.

⁶ U. S. Patent 1,287,605 (1918).

⁷ U. S. Patent 1,291,352 (1919).

⁸ Loc. cit.

Nature of Phosphatic Coating.

The coating formed in the Parker process is of a uniform dark gray color, varying in intensity of shade according to the surfacing treatment which the metal has previously received, such as sand blasting, tumbling, rubbing, etc. This coating is practically a constituent part of, or molecularly bonded to the metal and therefore cannot peel or be removed except by actual abrasion.

Upon close examination through a glass, the surface of the metal thus treated is found to be meshed with microscopic etching, which is said to form an excellent base for special finishes of enamel, paint or lacquer. Moreover, it is claimed that usually only one coat of such material need be applied to "Parkerized" surfaces.⁹ Ordinarily the processed materials when dry are dipped in a mixture of paraffin and oil, which changes the color of the coating from dark gray to a deep black.

The development of this process has made it possible to substitute iron and steel parts in machinery and equipment where formerly only copper, brass or some other metal resistant to corrosion could be used.

While this process is particularly applicable to automobile bodies and parts, ordnance, typewriters, etc., it is claimed that it can be successfully employed in treating machined work, sharp edged tools, dental needles, and other highly sharpened and tempered objects, without injuring or affecting their physical properties. Morrow¹⁰ states that the amount of building up on surfaces submitted to this treatment ranges from zero to less than 0.0003 inch.

Another advantage claimed for this rust proofing process is that the pores of the metal become filled with the phosphatic coating, and thus sometimes poor castings which might otherwise have to be discarded may be rendered tight and usable by submitting them to this rust proofing treatment.

Operation of the Process.

The following description of the method in which the rust proofing of iron and steel is carried out on a commercial scale is taken from the article of Eckelmann previously referred to.

"The iron or steel articles are freed from oil and grease by immersion for about twenty minutes in a solution of caustic soda or some patent cleaner—some of these cleaners easily removing mineral oils. Cleaning solutions should be over 200° F. for best results. The work

⁹ *Giving Metals a Rust Proofing Treatment*, Iron Age, Vol. 99, p. 587 (1917).

¹⁰ *Parkerizing—A Rust Proofing Process*, Amer. Machinist, Vol. 57, p. 361 (1922).

is now thoroughly rinsed in hot or boiling water, to dissolve any soaps formed in the cleaner, and when free of alkali passed into a 5 per cent H_2SO_4 pickle containing 1 ounce sodium bisulfite per gallon. The decomposition of this salt will liberate SO_2 and if the pickling solution is kept below 150°F. , the SO_2 will be retained in sufficient quantity to act upon the work being cleaned. Black scale often present on iron, mainly Fe_3O_4 , is quite insoluble, and can only be removed by excessive pickling, which is destructive to assembled or riveted work. The dissolved SO_2 will partly reduce the black scale to lower oxides, consequently facilitating solution and cleaning the metallic surfaces. When clean, which requires about 20 minutes, the work is again thoroughly rinsed in boiling water, to remove all acid and iron sulfates, then dried, sand tumbled or rubbed, and passed into the phosphate tank.

"It is essential at this point that all articles be free from any adhering sulfates, as this radical is harmful to the phosphate solution. Some will always remain on the work, particularly when many parts are massed and treated together, and the last traces must be removed by rubbing or tumbling with sand. Sulfates not only affect the action of the rust-proofing solution but cause the formation of a rough, glistening coating. This is a coarse crystalline phosphate of iron, apparently growing from nuclei at points previously covered with sulfates. The size of the surface crystals seems to depend not only on the amount of metallic sulfate present, but upon unequal acidity over the surfaces of the object treated.

"The writer has been able to eliminate the troublesome sanding operation in certain cases where the objects were of a shape permitting easy draining. After leaving the pickle the parts were immersed in lime-water, and the precipitated calcium sulfate removed by agitation in a hot-water rinse. When this procedure is possible much time can be saved. It is a point where further development is possible, and a closer study of the effect of the different pickling acids on the processing solution and finish is necessary.

"When metal is free from rust or scale, it can be sent to the phosphoric tank immediately after removing the grease and oil if a sand rub be substituted for the pickle. Clean, newly machined parts and stampings can be treated this way, the oil being removed with an organic solvent such as carbon tetrachloride. Unless the previous treatment of the steel or iron is known, this last procedure is not recommended.

"When clean the work is transferred from the wooden crates used for pickling to steel baskets used in the rust-proofing bath. When the sulfates are removed by limewater the time consumed in transferring the articles can be saved by using lead coated baskets of the largest possible mesh.

"Processing solution is made by mixing the phosphoric acid-iron phosphate mixture (sold under the trade name 'Hyroacid') and manganese dioxide in the proportions of 4 pints acid and 2 pounds MnO_2 to each gallon of water, thoroughly mixing and boiling. Prolonged boiling for 12 hours is necessary when the solution is first made up, to insure the correlation of the different variables, such as acidity, ferrous and ferric iron. Continuous circulation of the solution is effected by proper construction of the tank, which should be provided with side heating coils and deflection vanes. Sludge forming from MnO_2 after the tank has been in use for some time is prevented from coming in contact with the work by baffle plates placed a certain distance from the bottom of the tank.

"The articles are immersed from one to two and a half hours at 210° to 212° F. When the evolution of hydrogen has ceased, the work is removed, dried, dipped in a paraffine oil mixture, and set in racks or pans to drain. Between batches it is advisable to boil the solution for an hour or two, as this improves its action.

"Care must be taken to place the work so that it presents the least resistance to the flow induced by the heating coils and vanes in the tank.

"Iron and steel protected with phosphatic coatings are not so resistant to wear and abuse as sherardized or galvanized metal. Surfacing composed mainly of Fe_2O_3 produced by the Bower-Barff and similar processes are more resistant to acids and bluer in color. However, phosphatic rust proofing is considerable cheaper than any other well known rust proofing process in use to-day, the simplicity of treatment and uniformity being important factors in its favor."

Uses of Phosphates and Phosphoric Acid in Glass and Ceramic Products.

The chief uses of phosphoric acid in the glass and ceramic industries is for manufacturing optical, opaque and ornamental (translucent) glasses, bone china and enamel glazes. Although the quantity of phosphatic materials annually used for these purposes is relatively small when compared with the total consumption, nevertheless phosphates play an important rôle in imparting to the products of these industries certain desirable physical properties.

Optical Glasses—Phosphoric anhydride (P_2O_5) has been used to some extent in optical glasses to obtain the desirable properties of low dispersion and high refractive index.¹¹ These properties render a glass excellent for achromatizing with the Boro flints in the making of double objective lenses, which are used primarily to eliminate the sec-

¹¹ H. Hovestadt, *Jena Glass and its Scientific and Industrial Applications*, pp. 8-10, 1902.

ondary spectrum. Miethe¹² in 1888 made the first anastigmatic aplanat lens from a high phosphorous crown glass and a weak refracting flint. This was an important step in the elimination of spherical aberration. In 1889, Fritsch¹³ made a wide angled apochromatic lens of phosphate crown and borate flint. The barium phosphate crown glasses are very transparent to ultra violet rays.¹⁴

The following table¹⁵ (Table LVIII) gives some of the more important optical properties of the phosphate crown glasses.

TABLE LVIII
SOME OPTICAL PROPERTIES OF PHOSPHATE CROWN GLASSES

Type of Glass	Refractive Index	Mean Dispersion	Density
Light phosphate crown.....	1.5159	0.00737	2.58
Medium phosphate crown.....	1.5590	0.00835	3.07
Dense barium phosphate crown.....	1.5760	0.00884	3.35
Densest barium phosphate crown.....	1.5906	0.00922	3.66

The chemical composition¹⁶ of two typical phosphate optical glasses are given in Table LIX.

TABLE LIX
CHEMICAL COMPOSITION OF TWO TYPICAL PHOSPHATE OPTICAL GLASSES

No.	B ₂ O ₃	MgO	Al ₂ O ₃	As ₂ O ₃	K ₂ O	BaO	P ₂ O ₅
	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
1	3.0	4.0	10.0	0.5	12.0	0.0	70.5
2	3.0	0.0	8.0	1.5	0.0	25.0	59.5

Judging from the chemical composition of the phosphate glasses given in the above table it is to be expected that they would be somewhat soluble in water and hence weather quite readily. This is actually the case for even the moisture in a relatively dry atmosphere exerts a very marked corrosive action on such glasses. On this account phosphate lenses are used to a very limited extent at the present time, and when such glass is employed for optical purposes it is usually in cemented interior portions of complex lenses where it is protected from air and moisture.

¹² Vogel's Phot. Mitt., 25, pp. 123 and 173 (1888).

¹³ Phot. Korrespondenz, 26, p. 12 (1889).

¹⁴ Hovestadt, H., Jena Glass and Its Scientific and Industrial Applications (1902), p. 57.

¹⁵ Idem., pp. 8-10.

¹⁶ Idem., p. 132.

Opaque and Translucent Glasses.—The modern development of electrical illumination and the demand for indirect or diffused lighting has been largely responsible for the growth of the opaque and translucent glass industry.

Such materials as bone ash, pure phosphates, guano, magnesium, silicates, sodium and calcium fluorides, cryolite, fluosilicates, asbestos, tin oxide, etc., are used as opacifying agents. Alabaster glasses are probably the oldest type of the opaque glasses. They were first made in Bohemia¹⁷ and used principally for large jars, ornamental vases and perfume bottles. They contain high percentages of silica and small percentages of calcium, but no appreciable amount of phosphoric acid. The opacity of such glass was probably due to devitrification as the glass was made at relatively low temperatures.

With improvements in the heating system of glass furnaces, better methods and formulæ for making more permanent opaque glasses were sought. In 1743 Kunkel¹⁸ recommended the use of bone ash as an opacifying agent. He used a mix of 60 pounds sand, 40 pounds potassium carbonate and 10 pounds of bone ash. Calcined guano and in more recent years artificially prepared sodium or calcium phosphates have been used instead of bone ash, since these substances can be prepared very pure and in such a fine state of division that a more uniform and dependable glass can be obtained.

In the liquid state such glasses appear to be clear and transparent, but on cooling become an opaque white. The degree of opaqueness depends largely on the amounts of phosphate and silica present. A mixture low in silica requires less phosphate than one high in silica to produce the same degree of opaqueness.

Rosenhain¹⁹ and Scharrer²⁰ attribute the opacity of these glasses to small particles of calcium phosphate disseminated throughout the mass, the separation of this compound taking place as the glass cools.

On treating ground phosphate glass with dilute nitric acid, calcium phosphate goes into solution. This fact is cited as an indication that the calcium phosphate exists as such, in the glass mass.

These phosphate glasses, even though the white is very dense and opaque by reflected light may give a red or yellowish color to transmitted light. This undesirable property known as "fire," however, can be overcome by the addition of tin oxide to the batch.

Opal, opalescent and mother of pearl glasses occupy an important place in the ornamental glass industry. From the very beginning

¹⁷ Krak, J. B., *The Composition of Opaque Glasses*, *Glass Ind.*, **2**, pp 81-4 (1920)

¹⁸ Idem

¹⁹ Rosenhain, W., *Glass Manuf.*, p 184

²⁰ Abegg's *Handbuch der anorg. Chemie*, Vol. 3, pp. 2 and 391 (1907)

efforts have been made to produce a glass resembling mother of pearl.²¹ The earlier workers were concerned only in the decoration of glass with mother of pearl colors. The first iridescent glass appeared about 1870²² and since that time the progress has been very marked. Schwarzbach²³ gives the following batch mixture for one of the most successful of the mother of pearl glasses.

Sand	100	parts	by	weight
Potash	45	"	"	"
Red lead	52	"	"	"
Bone ash	8	"	"	"

By the addition of a small amount of manganese dioxide an excellent imitation of the antique Venetian mother of pearl is obtained. translucency and its pearly iridescence. J. W. Mellor²⁵ gives the following formula.

Sand	68	parts	by	weight
Potash	21	"	"	"
Soda	5	"	"	"
Red lead	5	"	"	"
Salt peter	1	"	"	"
Borax	1	"	"	"
Calc. spar	4	"	"	"
Bone ash	6-10	"	"	"

These typical formulae serve well to illustrate the importance of bone ash or phosphates in the glass industry.

Bone China.—Bone china is a development of the English potters, they having obtained their early information indirectly from China.²⁴ It is the most highly prized chinaware on the market, and also the most difficult to manufacture. The physical properties of bone china which appeal so strongly to the connoisseur are its fineness of texture, its translucency and its pearly iridescence. J. W. Mellor²⁵ gives the following interesting statement in regard to the bone china body. "Of all the different kinds of pottery bodies known to man, I believe that the so-called bone china body is the most remarkable.

"From the time the raw materials enter the blunger to the time the finished ware leaves the enamel kiln, the bone ash is the seat of a number of extraordinary chemical changes which make the chemistry of

²¹ Schwarzbach, O., *The Manuf. of Mother of Pearl Glass*, Sprechsaal, **53**, pp. 251-2 (1920). Translation in *Glass Ind.*, Vol. 2, pp. 7 and 8.

²² Idem.

²³ Idem.

²⁴ Mellor, J. W., *Trans. Eng. Ceram. Soc.*, **5**, p. 79 (1906).

²⁵ Mellor, J. W., *Trans. Eng. Ceram. Soc.*, Vol. 18, pp. 497-504 (1919).

the body unique. So far as I know there is nothing to approach it in the whole range of ceramics."

B. Moore²⁶ gives the composition of a normal English bone china as follows:

Bone ash	44	per cent
Cornwall stone ²⁷	30	" "
China clay	26	" "

The use of Cornwall stone, however, is objectionable owing to its variable composition, and therefore a mixture of feldspar and flint is often used to replace it. According to Moore the composition of good bone china (where feldspar is used) may fall within the following range:

Bone ash	42 to 32	per cent
Feldspar	15 to 19	" "
China clay	33 to 35	" "
Flint	10 to 14	" "

The materials should be finely ground (160 mesh) either separately or after mixing and then subjected to the action of powerful magnets to remove all traces of metallic iron.

The next operation, that of getting the body into the most plastic or workable condition requires considerable time and attention. It is, however, one of the most important steps in the whole manufacturing process for upon it depends the uniformity and fineness of texture so highly valued in the genuine bone china. Upon grinding Cornish stone or feldspar in water hydrolysis takes place and china clay and water glass are formed to some extent. In like manner the grinding of bone ash in water possibly forms some acid calcium phosphate or even phosphoric acid. As a result of this wet grinding the materials acquire a much greater plasticity.

It has been found advantageous to use a bone ash which has retained a large part of its carbon, as it is much more plastic than a hard burned bone ash.

The bone china body cannot be matured or tempered like an ordinary clay body,²⁸ because the organic matter in the bone ash will begin to putrefy with the development of small gas bubbles. Pug mills²⁹ cannot be successfully used, as the cutting action of the blades tends to make the clay short. The tempering should be accomplished more or

²⁶ Moore, B., *Eng. Ceram. Soc.*, **4**, p. 37 (1905).

²⁷ Cogswall stone is a highly silicious feldspar which varies considerably in composition.

²⁸ Mellor, J. W., *Trans. Eng. Ceram. Soc.*, **18**, pp. 497-504 (1919).

²⁹ Binns, C. F., *Trans. Am. Ceram. Soc.*, **12**, p. 175 (1910).

less by a kneading action. The French rolling table is said to more nearly meet these conditions, as it rolls and kneads the clay body without any cutting action. The rolls are covered with zinc so as not to contaminate the china body with iron.

Considerable skill is required in the working or molding of the body prepared and tempered as above. A number of the English factories still use the hand tool method³⁰ of molding the various pieces, however, the more enterprising manufacturers have developed molding machines which are even superior to the hand methods.

Skilled placers³¹ are required in placing the china for the "biscuit fire." For flat ware such as plates and saucers a burned flint bed, shaped to fit the piece, is used.

In the biscuit firing a tremendous contraction takes place up to a certain temperature. Great care must be exercised in this heating operation since excessive temperatures cause expansion and warping of the china and the formation of small bubbles in the ware. These bubbles are caused by the liberation of phosphorus from the bone ash in the body mixture.³² The reaction is analogous to that for the commercial preparation of phosphorus where bone ash, silica, and charcoal, are heated together at high temperatures.

The detrimental effects of iron are ordinarily manifested in the biscuit fire. While there is usually less than 1½ per cent of iron in the body, it is said this is very readily converted into iron phosphate if there is a reducing atmosphere in the oven caused by carbon in the bone ash, or through lack of air circulation in the kiln. The presence of this iron phosphate is shown by the blue or bluish green color of the ware.³³

This explanation as to the cause of the blue color, does not appear entirely satisfactory since sometimes a blue china is obtained in an oxidizing atmosphere where the bone ash contains very little carbon.

The carbon content of the bone ash may vary in character according to the manner in which it is calcined. If burnt rapidly at a high temperature the carbon will be left in a form which is slow and hard to burn out of the china body.

The composition of the china body, that is, the proportions of clay, bone, and stone in the mix requires a delicate adjustment to produce the right color effects, as for example where there is a large proportion of clay and a small proportion of stone, the tendency is to produce a blue or brown china. The proportion of bone ash is not so critical as

³⁰ Idem.

³¹ Idem.

³² Mellor, J. W., *Trans. Eng. Ceram. Soc.*, **18**, pp. 497-504 (1919).

³³ Idem.; Moore and Mellor, *Pott. Gazette*, **41**, pp. 1147-8 (1916).

that of the stone and clay. On the other hand where the proportion of stone is too high, the tendency is to blister or bloat. The higher fluxing powers of the stone also cause warping or sagging. The per cent of moisture in the clay is often a determining factor in the proper proportioning of the body materials.

On firing in the glost oven and enamel kiln these unstable phosphates ranging from the white variety to the blue or bluish green may oxidize to a brown or spotted brown stain. This oxidation may even take place years after, usually around the cracks in the glaze, where air may gradually seep through.

Crazing³⁴ seems to bear some relation to the brown stains, as it is most pronounced where the composition of the china is favorable to the formation of the bluish color, namely, that where the proportion of clay is high.

Blistering occurs most readily where the body has a high proportion of stone, which also means a higher percentage of alkali metals. This causes the mass to be soft and vitreous in the biscuit and glost ovens, thus hindering the escape of such gases as are present with the consequent production of minute bubbles or blisters in the finished ware.

Davis,³⁵ in experimenting with precipitated phosphates as substitutes for bone ash, found that the pure phosphates gave excellent results and that the failures so often blamed on the precipitated phosphate were due to the alkali impurities, thus pure alkali free phosphate gave as good results as bone ash. This suggested the use of Canadian apatites practically alkali free. Four bodies were made up according to the following formulæ using Canadian apatites:

	1	2	3	4
Apatite	42	39	35	32
Feldspar	15	16	17	19
China clay	33	34	34	35
Flint	10	11	14	14

All four of these bodies made excellent ware, number 4, however, showing the best translucency.

At the present time very little bone china is made in this country, but according to Binns³⁶ there is no definite reason why the industry should not be more firmly established in the United States as the demand for such ware is very great.

Porcelain Enamels and Glazes.—Tricalcium phosphate in the form

³⁴ Minute intersecting cracks on the surface glaze.

³⁵ Davis, N. B., Trans. Am. Ceram. Soc., 19, pp. 125-9 (1917).

³⁶ Binns, C. F., Trans. Am. Ceram. Soc., 12, p. 175 (1910).

of bone ash has an extensive use in the china and porcelain glaze industries. As early as 960 to 1279 A.D. the Chinese³⁷ (during the Sung dynasty) used considerable amounts of phosphate in their feldspathic glazes for pottery and porcelain. The following table (Table LX) gives the composition of several of these glazes:

TABLE LX
COMPOSITION OF SEVERAL EARLY CHINESE GLAZES

Glaze	SiO ₂	Al ₂ O ₃	CaO	K ₂ O or Na ₂ O	Fe ₂ O ₃	P ₂ O ₅
Hard glaze	70.3	10.6	5.9	5.0	2.3	7.2
Soft glaze	68.2	9.5	7.1	5.9	2.5	8.0
Light grayish green glaze	66.0	Fe ₂ O ₃ & Al ₂ O ₃ 13.0	6.8	8.3

Two of the more modern enamel glazes are shown in the following formulæ:³⁸

	No. 1 $\frac{1}{100}$	No. 2 $\frac{2}{100}$
Sand	60	30
Red lead	22	..
Potash	12	8
Bone ash	12	..
Tin oxide	5	3
Saltpeter	4	..
Borax	8
Soda	6
Lime	1/2
Arsenic

II. Fritz³⁹ states that most of the glazes containing P₂O₅ are subject to "crazing." He recommends the following batch mix to give a brilliant glaze free from this undesirable tendency.

K ₂ O	1 part
CaO	1 "
PbO	8 "
Al ₂ O ₃	2 "
P ₂ O ₅	20 "

Some of the most efficient colors for hard porcelains and glazes are metallic phosphates.⁴⁰ Cerium pyrophosphate gives a sulfur yellow

³⁷ Collie, J. N., Trans. Eng. Ceram. Soc., **15**, pp. 160-165 (1916).

³⁸ Schnuspehl, H., Die Glashütte, **37**, pp. 380-93.

³⁹ Fritz, H., Chem. Ztg., **42**, p. 422 (1918).

⁴⁰ Hertwig, T., Keram. Rundschau, **20**, p. 122.

color resistant to oxidizing and reducing gases. Ferric phosphate produces a chestnut brown. Manganese pyrophosphate gives a yellowish brown.

Cobalt phosphate and manganese phosphate or manganese dioxide yields a blue black color.

Cobalt pyrophosphate, aluminum phosphate, and zirconium pyrophosphate produce light blues. Tungsten phosphate gives a yellow color.

These ingredients are mixed thoroughly with oil and applied in thin coats before the final firing of the porcelain.

No statistics are available showing the quantities of mineral phosphates and bone products used in the manufacture of glass, bone china, and porcelain glazes.

"The Use of Phosphoric Acid in Beverages."

With few exceptions all manufactured beverages or "soft drinks" contain a small percentage of acid as one of their constituents. Without the addition of an acid, most beverages, particularly those made up with natural or artificial fruit flavors, lack that quality of "sharpness" which the consumer finds so palatable.

The acids which have been suggested or are actually being used to impart the desired acidity of "sourness" to soft drinks fall into two general classes.

1. Organic acids such as acetic, citric, tartaric and lactic, all of which are present or formed in food products.

2. Inorganic or mineral acids such as sulfuric, hydrochloric and phosphoric, all of which are produced on a large scale from inorganic materials.

The term "acidity" in a chemical sense ordinarily means the neutralizing strength of an acid in terms of a standard alkali solution or the quantity of "acid" hydrogen present. This, however, is not a true measure of the strength of an acid since the activity of the acid hydrogen varies in different types of acid. The most accurate and general recognized method of measuring the *intensity* of acid solutions to-day is by the determination of their hydrogen ion (P. H.) concentrations. This method is fully and ably treated in a number of standard text books and scientific articles and therefore its discussion is not warranted here.

Acidity as understood by the manufacturer and bottler of soft drinks, however, is the degree of "sourness" (as determined by taste) imparted to a beverage by equivalent quantities of acid hydrogen fur-

nished in the form of the acids enumerated above. He is interested particularly in obtaining this desired acidity in the cheapest possible form, provided the acid employed is pure, digestible and does not detract in any way from the wholesomeness of his product.

In the following table (Table LXI) prepared by Skinner and Sale⁴¹ the relative cost of this so-called "sourness" in the form of the various organic and inorganic acid used in the manufacture of soft drinks are given.

In the first column are given the types of acid and the strength of the commercial articles offered on the market. In column 2 are given the pounds of these commercial grades employed in 100 gallons of a 1/100 normal acid solution which is approximately the acidity of the average modern soft drink. In column 3 the relative sourness of such dilute standard acid solutions is given—this degree of sourness being determined by taste. In column 4 are given the weights in pounds of the various acids (commercial grades) which must be added to 100 gallons of water or solution to give equal sourness to a beverage.

TABLE LXI
RELATIVE COST OF SOURNESS IN THE FORM OF VARIOUS ACIDS *

Name and Commercial Grade of Acid	Lbs. of Acid per 100 Gal. of N/100 Solution ^b	Relative Sourness of N/100 Solution	Lbs. of Acid per 100 Gals. of Solution of Equal Sourness ^c	Current Prices of Acid per Lb.	Cost of Sourness per 100 Gals. of Beverage ^d	Cost of Sourness per ½ Pint of Beverage
				Cents	Cents	Cents
Acetic acid (56%)...	0.894	70	1.276	7.6	9.7	0.006
Lactic acid (40%)...	1.878	100	1.878	39.0	73.2	0.045
Citric acid (91%)...	0.587	100	1.587	100.0	58.7	0.036
Tartaric acid (99.5%)	0.629	100	0.629	85.0	53.4	0.033
Phosphoric acid (50%)	0.818	120	0.681	22.0	15.0	0.008
Sulphuric acid (95%)	0.430	200	0.215	16.5	3.5	0.002
Hydrochloric acid (37%)	0.823	200	0.411	19.5	8.0	0.005

* Table taken from article by Skinner and Sale, *Acids in Beverages*, Nat. Bottler's Gazette, p. 67, July 5, 1920.

^b Bottled soda of the ginger ale type has an acidity and sourness approximately equal to N/100 solution of citric tartaric or lactic acid. The solutions compared in this column are of equal acidity but not of equal sourness.

^c The degree of sourness of these solutions is approximately the same as the sourness of bottled soda of the acid type (N/100 solution of citric acid).

^d The price of all the acids enumerated is now considerably lower^a than at the time this article was published.

^a *Acids in Beverages*, Nat. Bottlers' Gazette, p. 67, July 5 (1920).

Finally, in the last two columns the cost of this acidity or sourness (at the then current prices) per 100 gallons and per $\frac{1}{2}$ pint bottle is given.

It will be noted that acid solutions of equal normality (having the same acid hydrogen content) differ very materially in sourness—the inorganic acids having a much more pronounced acid taste. The cheapest sources of this sourness were found to be sulfuric, and hydrochloric acids, with acetic acid third and phosphoric acid a close fourth. The cost of this same degree of acidity in the form of the other organic acids is from four to eight times greater than in the form of phosphoric acid.

The use of all the organic acids enumerated above is approved by the Bureau of Chemistry, U. S. Department of Agriculture, since they are naturally present or formed in food products to which the human digestive tract is accustomed. The presence of these acids in beverages, therefore, according to Skinner and Sale⁴² "is quite proper and advisable."

Of the three inorganic acids mentioned, however, only phosphoric acid is generally accepted as a wholesome ingredient of soft drinks. The employment of sulfuric and hydrochloric acids in food products according to the authorities cited above "is a comparatively recent development and is questionable to say the least, being considered very undesirable by many."

Phosphoric acid has been employed for many years in the preparation of so-called phosphate beverages such as orange, lemon and cherry phosphates. In recent years the use of this acid has grown in favor and it now constitutes a part or the whole of the acid constituent of a number of fruit flavored beverages as well as those of the cola type.

The increased use of phosphoric acid is due not only to the relatively low cost of this compound but to the fact that it has a certain recognized medicinal value. Moreover, compounds of phosphorus play an important rôle in the human diet and it is argued that acidity furnished in the form of orthophosphoric acid is certainly not deleterious and probably beneficial to health.

No accurate figures are available showing the quantity of phosphoric acid consumed in beverages, but it is unquestionably very appreciable. Of the 4,000,000,000 half pint bottles of soft drinks annually consumed probably three-fourths have citric and tartaric acid as their acid constituents. Assuming that one-half of the remainder or 500,000,000 bottles contain phosphoric acid (2 grains to each bottle), we obtain a figure of 110,000 pounds of H_3PO_4 or 220,000 pounds of 50 per cent H_3PO_4 , which is the usual strength in which it is sold to the trade.

⁴² Loc. cit.

This does not take into consideration the fruit syrups and phosphate drinks sold at the soda fountains, which would probably add at least 100,000 pounds more, giving a total consumption of 320,000 pounds of 50 per cent H_3PO_4 or 160 tons per annum.

In addition to its use in beverages, small percentages of phosphoric acid are used to impart acid flavor to jams and jellies⁴³ manufactured on a large scale. No objection is offered to its employment for these purposes by the pure food laws. It is needless to say, however, that the acid used for food purposes must be very pure and free from such deleterious substances as arsenic and salts of copper, lead, etc. The purification of phosphoric acid has been described in a previous chapter.

"Phosphoric Acid in Dental Cements."

Phosphoric acid is widely used as one of the constituents in dental cements. While the actual quantity thus annually consumed necessarily must be relatively small, this acid nevertheless performs an important function in modern dentistry and there is every indication that its use for this purpose will continue to increase.

Much careful and painstaking research has been conducted in seeking and in choosing materials best suited to stand up under the deteriorating conditions to which dental cements are exposed. Not only must such cements withstand severe strains and stresses, but also be subjected to chemical and bacterial influences tending to bring about their disintegration.

When we consider the following conditions, which all good dental cements should meet, it is easy to see what a wide field of research is open to the physicist, chemist and bacteriologist:

- (1) Relatively quick setting and strong adhesive properties.
- (2) A coefficient of expansion practically identical with that of the human teeth.
- (3) Hardness and a high crushing strength.
- (4) The property of being nonporous and resistant to the solvent effect of saliva.
- (5) Germicidal properties.

In addition to the above properties, certain types of cements must have a color and translucency simulating the lifelike appearance of natural teeth.

While their minor ingredients vary somewhat the bulk of the dental cements may be divided into two general classes.

⁴³ Meckstroth, J. T., *Industrial Uses of Phosphoric Acid*, Chem. and Met. Eng., Vol. 26, p. 223 (1920).

- (1) Oxyphosphate cements consisting largely of oxyphosphate of zinc.
- (2) Silicate cements, which are composed of basic aluminum silicates and phosphates with smaller amounts of lime magnesia potash and soda.

A third class of cements containing varying percentages of copper compounds (mainly oxides) are also produced, which have more marked germicidal properties⁴⁴ than the two classes mentioned above. These copper cements are used in filling cavities and nerve channels, which are difficult to thoroughly clean. Cements containing silver phosphate are also employed for this same purpose, but since both copper and silver salts produce dark colored cements, their use is largely confined to posterior teeth or to cementing crowns and caps where the cement will not be conspicuous.

Dental cements reach the dentist in the form of a powder and a liquid to be mixed by him when he is ready to use them. The powder or solid contains chiefly basic materials and the liquid furnishes the acid ingredient. Vogt⁴⁵ and Poetschke⁴⁶ lay great emphasis on the importance of thoroughly mixing these materials and the consistency of the paste which is formed, pointing out that both the chemical constitution and the physical properties of the final product are dependent upon the most intimate contact between the reacting ingredients.

Oxyphosphate Cements.

The main ingredient of the powdered portion of the oxyphosphate cements is zinc oxide, which has been calcined to render it less active towards phosphoric acid. A small quantity of bismuth oxide is sometimes added to the zinc oxide before calcining since this compound tends to make the cement impervious to saliva. Silica or quartz flour is also one of the constituents of the oxyphosphate powders, but merely acts as a filler just as sand and gravel are employed in concrete mixtures.

The liquid portion of the cement consists of a relatively strong solution of phosphoric acid to which has been added zinc oxide, hydrated alumina or some other basic material to partially neutralize the acid and cause it to act more slowly, when mixed with the cement powder. The time of setting is thus sufficiently delayed to permit the thorough mixing of the ingredients before the cement is placed in the tooth.

⁴⁴ Poetschke, Paul, *Germicidal Efficiency of Dental Cements*, J. Ind. & Eng. Chem., Vol. 7, p. 195 (1915); Smirnow, M. R., *Germicidal Properties of Dental Cements*, Dental Cosmos, Vol. 57, p. 1209 (1915).

⁴⁵ Silicate Cements, *Dental Items of Interest*, Vol. 42, p. 329 (1920).

⁴⁶ Physical Properties of Dental Cements I and II, Ind. and Eng. Chem., Vol. 8, p. 309 (1916) and Vol. 15, p. 341 (1923).

Upon mixing the acid and base, zinc phosphate is produced, which becomes converted shortly into the hydrated or crystalline form. It is the formation of this crystalline zinc phosphate, which gives the cement its adhesive and setting properties. The base and acid should be so proportioned that a thick paste is produced, thereby insuring the presence of an excess of zinc oxide and the absence of free acid in the final product. It is also important that the cement should set relatively slowly at ordinary temperatures, but that the rate of setting be accelerated at somewhat elevated temperatures. In this way the dentist has ample time to mix the ingredients, but the patient will not be inconvenienced in waiting for the cement to harden. According to Poetschke⁴⁷ the setting time for properly prepared oxyphosphate cement is approximately 3 minutes at 70° to 80° C.

The oxyphosphate cements when free from copper or other colored compounds are hard and white, but quite opaque and hence unsuitable for filling or facing the anterior teeth. These cements, therefore, are used for cementing crowns, caps, bridges, inlays and facings and as fillings, mainly in the posterior teeth.

The Silicate Cements.

The silicate cements were developed to meet a long felt want for a material with adhesive and setting properties, which would also have a color and translucency approximating that of natural teeth.

While such cements have not been entirely perfected, they have been greatly improved, both in regard to their appearance, as well as in their other physical properties.

The solid or powdered portion of the silicate cements consists chiefly of basic aluminum silicates, with smaller percentages of lime, magnesia, soda and potash.

Wright⁴⁸ gives the following analyses of four synthetic silicates, making up the powdered portions of dental cements.

TABLE LXII

COMPOSITION OF THE POWDERED PORTION OF FOUR SILICATE DENTAL CEMENTS

Ingredients	No. 1	No. 2	No. 3	No. 4
Silica (SiO ₂)	40.26	36.91	44.00	37.00
Alumina (Al ₂ O ₃)	50.62	33.69	41.00	32.20
Lime (CaO)	5.00	7.26	2.00	7.50
Magnesia (MgO)51
Potash and soda (K ₂ O and Na ₂ O)....	1.08	15.88	13.00	10.10
Phosphorus pentoxide (P ₂ O ₅).....	4.00	1.90
Fluorine (F ₂)	9.30

⁴⁷ Loc. cit.

⁴⁸ Study of Some Dental Cements, J. Dental Research, Vol. 1, p. 35 (1919).

The silica and alumina content of two of the above powders (Nos. 2 and 4), however, do not fall within the limits set by W. and D. Asch⁴⁹ as necessary for silicate cements. These investigators give these limits as follows:

(1) Alumina (Al_2O_3)	38 to 50 per cent
Lime (CaO)	6 to 12 " "
Silica (SiO_2)	40 to 44 " "

The solid or powdered portion of a silicate cement is produced by first intimately mixing the finely ground ingredients and then fusing the mass at a temperature varying from 2000° to 2500° F. After cooling, the melt is ground in a ball mill, sieved and put up in tightly closed containers for the market.

The liquid portion of the silicate cements with which the solid ingredient is mixed, also consists of phosphoric acid to which hydrated aluminum oxide or phosphate has been added to cut down its activity towards the silicate powder. According to Vogt⁵⁰ the main difference between the acid solution used in zinc cement and that employed in the silicate type is that in the latter case the concentration or specific gravity of the solution is lower.

Poetschke⁵¹ found that the use of an acid solution with a specific gravity of 1.558 at 15° C. gave cements which had the highest crushing strength. More dilute acid solutions produced cements less resistant to the action of saliva and the use of more concentrated acid gave cements which were not only weaker, but more soluble under oral conditions. Wright⁵² states that the use of less concentrated acid solutions causes the silicate cements to set somewhat faster than where stronger acid is employed. This may be an advantage in the case of cements of this type, which are apt to set very slowly and thus cause the patient some inconvenience.

Experience has shown, therefore, that a uniform composition and concentration of the acid solution is of great importance for each type of cement powder employed if concordant results are to be obtained.

Since little is known of the manner in which the various ingredients of the silicate powders are combined, there is considerable difference of opinion regarding the chemical reactions involved when such powders are mixed with the solution of phosphoric acid.

Some believe that the first reaction is merely that of hydrating the

⁴⁹ Silicates in Chemistry and Commerce (1913)

⁵⁰ Loc. cit

⁵¹ Loc. cit

⁵² Study of Some Dental Cements, J of Dental Research, Vol 1, p. 35 (1919)

calcium alumino-silicate, with the subsequent replacement of the water by the acid radical (PO_4).

Vogt⁵³ says that the reactions resulting from the mixing of phosphoric acid and a silicate powder take place in two stages, resulting in a primary and secondary setting. He thinks that the first setting (which takes place in about 8 minutes) is due to a reaction similar to that occurring in the zinc oxyphosphate cements—namely, the formation of hydrated phosphates of aluminum and other bases. The second or final setting, however, extends over a much longer period and while not sharply defined is regarded as due to the gradual combination of water with certain complex aluminum silicates. This is practically the same reason offered in explaining the setting of Portland cement.

In any event Vogt recommends that the silicate cements when freshly applied be protected from moisture until they assume hydraulic properties. He states that while sometimes silicate fillings are finished at a single sitting, it is better practice to cover them with a waterproof coating and polish and finish them 24 hours later.

Properly proportioned and carefully mixed silicate cements may be employed as fillings and facings in the anterior teeth, but the possibility of improving the adhesive and resistant properties of such cements still offers a fertile field for research.

Phosphoric Acid and Phosphates in Photography.

Salts of phosphoric acid are used to a limited extent in photographic processes. Di- and trisodium phosphates, monopotassium phosphate and silver phosphate are the salts most generally employed, but monosodium, uranium, manganese, barium and vanadium phosphates have been used in minor quantities though largely in experimental research work.

Free phosphoric acid is employed in the so-called "Aniline Process" for the reproduction of line subjects. This process, which was invented by Willis,⁵⁴ is based on the property of bichromate of potash forming with aniline salts dark colored precipitates. The printing paper is coated with a solution of potassium bichromate to which phosphoric acid has been added. After exposure the development of the images or outline is effected by submitting the paper to the action of aniline vapors.

The sensitiveness to light of silver phosphate was discovered by Stromeyer⁵⁵ as early as 1830, and this property of the salt was first

⁵³ Loc. cit.

⁵⁴ Eder's Handbuch, Vol. 4, p. 275 (1900).

⁵⁵ Cassell's Cyclopedia of Photography, p. 401 (1912).

applied to photography by Dr. Fyfe⁵⁶ in 1839, when he made a light sensitive paper by soaking it in a solution of sodium phosphate, drying and then coating one surface with silver nitrate and then again immersing in the solution of sodium phosphate. Silver phosphate in addition to its light sensitiveness is quite insoluble and it is these two properties which make it suitable for use in emulsions for printing-out and developing-out papers. Schwartz⁵⁷ prepared an emulsion using twice as much disodium phosphate as is necessary to convert the silver nitrate into phosphate, and added potassium chlorate and citric acid with a little chrome alum to harden the film. Such an emulsion is said to be rapid, and easily developed, giving an image of metallic silver having a wide range of tones and the permanence of bromide prints.

Schwartz⁵⁸ also has patented an emulsion consisting of gelatin, silver phosphate, chromate and an organic silver salt. In his U. S. Patent No. 916,616 (1909) he describes a photographic paper prepared by applying first a protective layer of a phosphate of zinc or an alkaline earth metal. The silver emulsion is then spread over this phosphate layer, the silver salts diffusing into the ground forming insoluble compounds.

Silver phosphate is also used in the "Iron Silver Process"⁵⁹ in conjunction with a light sensitive organic ferric salt such as ferric oxalate. When the sensitized plate or film is exposed to light, two distinct photo-chemical reactions take place, viz., the ferric salt is reduced to ferrous salt in proportion to the amount of light received, and the silver phosphate which possesses all the properties required for the production of a perfect image is at the same time affected also in proportion to the amount of light received. When these reactions have taken place, the ferrous compound produced will act as a developer for the silver compound in the presence of the alkali salt of the organic acid present, and thus the amount of the developer is automatically proportionate to the amount of exposure which has taken place.

Trisodium phosphate was first suggested by Lumière⁶⁰ as a substitute for alkali metal hydrates or carbonates in alkaline developers. He also proposed the use of trisodium phosphate in the simultaneous development and fixing⁶¹ of photographic images. The following formula is given:

⁵⁶ Idem; Willson's *Cyclopedia of Photography*, p. 274 (1899).

⁵⁷ Sensitive Silver Phosphate Paper, *Bull. soc. franc. phot.*, 25, p. 163.

⁵⁸ U. S. Patent Reissue 13,162

⁵⁹ Schwartz, Y., *Iron Silver Process*, *Brit. J. Phot. Almanac*, p. 382 (1923).

⁶⁰ Cassol's *Cyclopedia of Photography*, p. 501 (1912).

⁶¹ Lumière, A. and L., *Seyewetz, A., Improvements in Methods for Simultaneous Development and Fixing of Photographic Images*, *Bull. Soc. Franc. Phot.*, 7, pp. 234-8 (1920). *Simultaneous Development and Fixing*, *Bull. Soc. Franc. Phot.*, 8, pp. 220-1 (1921).

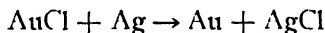
1,000	cc. of water
32	grams of sodium sulfite
40	" " "Hypo"
6	" " metaquinone
100	" " trisodium phosphate.

While a generous exposure is usually necessary, the results of using simultaneous developing and fixing baths are claimed to be not only as good as where separate developing and fixing baths are employed, but the danger of overdevelopment is materially reduced.

The use of trisodium or tripotassium phosphates in developers is based on their alkalinity. The disodium or dipotassium salt may be used, however, in conjunction with free alkali, since the actual function of the phosphate ion is that of a buffer; regulating the acidity or alkalinity of the bath.

The principal value of alkaline phosphates in this connection is in developers intended for use in tropical climates. It is possible to use a high concentration of the alkaline phosphate and obtain the well known salt depressing action on the swelling of gelatine, which thus reduces the chances of the emulsion softening or dissolving at the higher temperatures.

Disodium or dipotassium phosphate finds its most extensive photographic use in gold toning baths for printing out papers. Gold toning⁶² is accomplished by the substitution of metallic gold for the metallic silver in the printed out image, according to the following reaction:



This reaction takes place best under neutral or slightly alkaline conditions. The dialkaline phosphates are often used to furnish the necessary alkalinity.

Another use for disodium phosphate is in certain developing solutions⁶³ where it has a marked retarding effect.

"Phosphates in Fireproofing Compounds."

The sodium and ammonium salts of phosphoric acid are employed as ingredients in a number of fireproofing compounds.

It was long ago noticed that old timbers which had been used in buildings where phosphoric acid and phosphate salts were manufac-

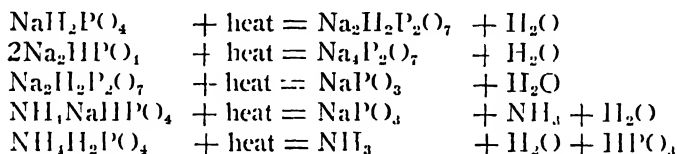
⁶² Cassel's *Cyclopedia of Photography*, pp. 279 and 544 (1912); Föder's *Ausführliches Handbuch der Photographie*, 4, p. 8 (1900); Willson's *Cyclopedia of Photography*, p. 27 (1899).

⁶³ Cramer, H. Lapps, *Phot. Korr.*, Vol. 52, pp. 35-36 (1915).

tured and which become impregnated with phosphate compounds could only be burned with great difficulty. The resistance to fire of such material, which is ordinarily readily combustible, first suggested the idea of using phosphates to treat wood and fabrics for the purpose of rendering them fireproof.

The several soluble inorganic compounds employed as fireproofing agents are sodium silicate, borax, magnesium sulfate, ammonium sulfate, ammonium phosphate, sodium phosphate and sodium acid pyrophosphate.

One of the main reasons given to explain why salts of ortho- and pyrophosphoric acid have fireproofing properties is the fact that on heating to high temperatures, they decompose yielding water, and in the case of ammonium salts ammonia gas is driven off, which forms a non-oxidizing atmosphere around the heated surface. The reactions involved in heating the various phosphates of ammonia and soda may be represented thus:



The residual material—normal sodium pyrophosphate, metaphosphate and metaphosphoric acid are fusible compounds, which tend to form glazes, thus further protecting the surfaces of combustible material from the action of the flame.

Ferguson⁶⁴ employs a solution of four ingredients mixed with water in the following proportions:

Sodium Silicate (Na_2SiO_3)	= 143 Parts
Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)	= 10 "
Microcosmic Salt ($\text{NaH}_2\text{N}_2\text{P}_2\text{O}_7$)	= 10 "
Monosodium Phosphate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$)	= 4 "
Water	= 100 "

Sodium silicate is used in this mixture because of the refractory nature of the glaze, which it forms. Borax is employed because of its well known property of fusing to a glass at high temperatures, and the inventor also claims that it aids in distributing the fireproof film of sodium silicate. In addition to the fact that the phosphate salts have fireproofing properties, sodium ammonium phosphate gives off ammonia

⁶⁴ U. S. Patent No. 1,271,506 (1918).

when heated and it is claimed that this ammonia is held for a short time beneath the fireproof film of sodium silicate and borax, serving not only to extinguish the flame, but also the smoldering embers.

Landau⁶⁶ proposes to prevent the decay of wood and at the same time render it fireproof, by treating it with a solution containing trioxymethylene and inorganic salts, such as ammonium phosphate, ammonium sulfate, ammonium borate and magnesium sulfate.

A fireproof paint for coating wood, metal, or even fabric is the subject of a patent issued to Wortelmann⁶⁶ in 1921. The composition of this material is approximately as follows:

Water	= 40 Parts
Sodium Silicate (40° Bé.)	= 60 "
Powdered Asbestos	= 60 "
Sodium Phosphate	= 2 "
Magnesium Sulfate (10 per cent sol.)	= 2 "
Saponified Resin (10 per cent sol)	= 2 "
Glycerine	= 1 "

A mixture of the above composition, while unquestionably giving fire resisting coating would hardly do for fabrics, since it contains so much insoluble material, that the pores of most materials would be filled up and their appearance impaired.

Such a coating also could probably only be employed for inside work because of the water solubility of all but one of the ingredients.

One of the great objections raised to the use of solutions of inorganic salts as fireproofing agents, is their tendency to crystallize and drop from the treated surface as fine crystals or powder. Moreover, in the treatment of fabrics, most of these fireproofing compounds tend to stiffen the fabrics, and prevent curtains, draperies, etc., from hanging in natural graceful folds.

With the idea of overcoming these objections, Andrews and Mathias⁶⁷ after a series of investigations, proposed the use of solutions containing monosodium phosphate and borax, or disodium phosphate and boric acid, so proportioned that the dried mixture is non-crystalline and has a pliable or colloidal nature, which causes it to adhere to fabrics, without stiffening them. These investigators prefer to use the phosphates of soda instead of ammonia particularly on fabrics because of the fact that the latter salts, tend to lose ammonia and hence the fireproofing compound not only becomes less effective, but gradually

⁶⁶ U. S. Patent No. 1,274,171 (1918).

⁶⁷ U. S. Patent No. 1,397,028 (1921).

⁶⁸ U. S. Patents 1,501,895 and 1,501,911 (1918).

assumes an acid nature, which deteriorates the fibre and injures the color of dyed materials.

For certain purposes the application of coatings on cloth or fabric, which are both fireproof and waterproof is of very great importance. An outstanding case is the fabric employed in making the wings of aeroplanes.

In order to render such fabric, impervious to air and moisture, it is customary to coat it with such substances as pyroxylin or acetyl cellulose, which not only renders the material waterproof, but causes enough shrinkage to tighten the fabric on the frame. These coatings, however, are highly inflammable, which adds greatly to the hazards of aviation and hence a method of fireproofing or lessening their inflammability is of considerable importance.

Lindsay⁶⁸ proposes to use both an organic and inorganic phosphate for this purpose. The materials employed and the method of application may be briefly described as follows:

The fabric is first fastened to the aeroplane frame and a solution of ammonium phosphate applied with a brush till the fibres are thoroughly impregnated with the salt. After drying, the following solution is applied to the cloth.

Pyroxylin	100 parts
Tricresyl phosphate	50 "
Acetone	300 "
Methyl Alcohol	600 "
Amyl Acetate	300 "

Several coats of this solution may be used if necessary to obtain the desired effect.

The tricresyl phosphate is said to materially reduce the inflammability of the pyroxylin so that this type of coating even without the addition of the ammonium phosphate is safer than that previously employed. The presence of fine crystals of ammonium phosphate in the fibres of the cloth, however, and their distribution through the mass of pyroxylin increases still further the fireproof properties of the fabric.

Since the ammonium phosphate is coated with the waterproof pyroxylin the inventor claims that there is no danger of the salt being washed away or lost on exposure to the weather.

It is not known to what extent phosphates are now used for fireproofing purposes, but their consumption will probably constantly increase.

⁶⁸ U. S. Patents Nos. 1,523,813 and 1,523,814 (1925).

Phosphoric Acid and Phosphates in the Refining of Sugar.

Phosphoric Acid as a Defecating Agent.

In the preliminary treatment of fresh cane or beet sugar juice it is necessary to add a defecating agent to remove fibrous and albuminoid matter, neutralize certain organic acids and thus prevent fermentation and subsequent inversion of the sugar when the juice is boiled.

Thus defecation is brought about by heating the juice with milk of lime which on boiling produces a thick scum or precipitate of lime salts. Ordinarily the quantity of lime employed is from 0.2 to 0.3 per cent of the weight of the juice, but the amount added should be carefully controlled since an excess of this base causes the sugar solutions to grow dark on boiling due to the decomposition of glucose, etc.

Sugar solutions which have been heavily limed must be treated with an acid in order to neutralize them and at one time monocalcium phosphate in the form of a thick paste was extensively employed for this purpose. While a limited quantity of this so-called "phosphoric acid paste" is still used to correct the alkalinity of sugar juice it has been found that this neutralization can be brought about as efficiently and more economically by the use of sulfur dioxide.

A number of patented products, however, having monocalcium phosphate as their base are now on the market, but while they are employed partly for the purpose of neutralizing alkalinity of the juice their chief function is to promote subsidence of the non-sugars and colloidal material present in suspension. For this purpose lime cream (milk of lime) is employed along with the acid paste with the result that a dense precipitate of tricalcium phosphate is formed which carries down with it the lighter organic precipitates and colloidal material which otherwise are very difficult to remove. The clear juice is then drawn off and sent to the evaporators for concentration and subsequent crystallization into raw sugar.

The use of phosphoric acid and lime as defecating agents had become pretty general as far back as 1888,⁶⁶ as it was found that the precipitate of phosphate of lime improved the color and the rate of filtration of the juice. With the more general use of the filter press instead of the old bag filters employed at that time, diatomaceous earth has come more and more into favor as a clarifying medium. For wash syrup and other low-grade sugar solutions the phosphoric acid-lime treatment is still preferred because of the type of precipitate formed.⁷⁰

⁶⁶ Wamford and Newlands, *Sugar*, p. 622 (1888).

⁷⁰ Perkins, H. Z. E., *Cane Sugar Refining at the Present Day*, Louisiana Planter Reference Book, Vol. II, p. 39 (1924).

In a recent investigation conducted by the Hawaiian Sugar Planters Association ⁷¹ it was found that juices of low phosphoric acid content do not clarify well. Juices which contain less than 0.03 per cent of P_2O_5 gave cloudy solutions while those containing over this amount of P_2O_5 gave clear solutions. It is recommended to add phosphoric acid where the quantity present is subnormal. Needless to say that phosphoric acid and phosphates used for the purification of sugar solutions must be free from arsenic, lead and other objectionable impurities.

Another process of defecating sugar solutions by the use of a salt of phosphoric acid was proposed by Legrange, ⁷² a French chemist, about 1880.

This process, the apparent purpose of which was to obviate the use of lime, was carried out as follows:

To the boiling sugar juice a sufficient quantity of a solution of barium hydroxide was added to carry down the sulfate present. This treatment was immediately followed by the addition of triammonium phosphate which carried down a precipitated mixture of tribasic calcium, magnesium and barium phosphates.

Since triammonium phosphate is quite an unstable compound, such a process is somewhat awkward and in the more recent treatises on the production and refining of sugar no mention is made of this method of purification being practised at the present time.

Demerara Crystals.

Phosphoric acid or monocalcium phosphate is also employed in the production of a type of unrefined cane sugar having a light yellow color, pleasing odor and delicate flavor. This sugar is sold under such names as coffee sugar, yellow sugar, and Demerara crystals. Its manufacture entails the preservation of the physical characteristics of the cane juice and the retention of certain aromatic substances, which the raw liquor contains.

In producing this type of sugar the cane juice is first saturated with sulfur dioxide at ordinary temperatures. This sulfited juice is then pumped through a steam heater and the temperature raised to 212° F. The juice then goes to a settling tank, where it is treated with lime. After the impurities have settled the relatively clear juice which is of a dark green color is run into what is known as an eliminating pan provided with heating coils and a gutter surrounding the upper part into which the froth is skimmed. The juice is brought to a boiling temperature and phosphoric acid added, which changes the color of the

⁷¹The Clarification of Cane Juices, Facts About Sugar, Vol. 19, pp. 610-16 (1924).

⁷²Lock, Wigner and Harland, Sugar Growing and Refining, pp. 372-373 (1882).

solution from green to a canary yellow by liberating the coloring matter from its combination with the bases in the juice. After skimming off the froth the juice goes to the multiple effect evaporators and hence to the crystallizing pans.

Animal Charcoal.

The most important phosphate product used in the manufacture of sugar is animal charcoal, the function of which is to decolorize, purify and sterilize the sugar solution preparatory to its concentration and final crystallization into refined sugar.

No substance has yet been discovered for this purpose which combines the desirable physical and chemical properties of animal charcoal. It is true that activated carbons have been developed which weight for weight exert a far greater decolorizing effect on sugar solutions than animal charcoal, but these must be used on cloth filters since they are not in combination with a porous structure such as the calcium phosphate of charred bone. Moreover, these activated carbons are expensive, the losses are often heavy and they do not remove appreciable quantities of dissolved mineral matter which is one of the important functions of animal charcoal.

Animal charcoal exerts a threefold action on sugar solutions.

- (1) The phosphate content of the char removes a considerable portion of the dissolved mineral matter from the solution, the presence of which is apt to effect unfavorably the crystallizing power of the concentrated syrup.
- (2) The carbon absorbs the coloring matter, dissolved iron salts, and organic impurities such as gums and uncrystallizable sugars.
- (3) The char effects a sterilization of the sugar solution by the absorption of microorganisms.

While animal charcoal may be made from bones, dried blood, leather, horns or other animal products, the char which is used to purify sugar solutions should always be produced from high-grade bones.

These bones are first crushed and then degreased, either by boiling or by means of a fat-extracting solvent. The degreased bones are then placed in cast iron retorts which are heated to bright redness for eight to twelve hours. The by-products of this destructive distillation (combustible gas ammonia, bone oil and pitch) are collected and utilized for various purposes.

The charred bones are discharged into metal containers which are immediately sealed to prevent the oxidation of their carbon content. After the char has cooled it is removed from the containers, crushed and screened—the coarser particles (between $\frac{1}{8}$ inch and $\frac{1}{40}$ inch) going

to the charcoal filters and the finer portion, or dust, being used in the manufacture of phosphoric acid. Magnetic separators are sometimes employed to remove iron and steel from the crushed product.

Before being used as a purifying agent, however, it is usually necessary to remove any absorbed gases and soluble mineral matter retained by the bone in the charring process. Accordingly the granular charcoal is thoroughly washed with hot water, drained and again heated but to a considerably lower temperature than that employed in the first instance.

The following analyses, according to G. Fairrie,⁷³ is typical of a high-grade stock char at the beginning of its use in the refinery.

Carbon (C)	10.68	per cent
Carbonate of lime (CaCO_3)	7.90	" "
Sulphide of lime (CaS_2)	trace	" "
Sulphate of lime (CaSO_4)26	" "
Phosphate of lime (Ca_3PO_4) ₂	80.25	" "
Oxide of iron (Fe_2O_3)10	" "
Silica (SiO_2)81	" "
Total	100.00	

The crushed, sieved and washed charcoal is then carefully packed in cast iron cylindrical filters from 30 to 50 feet in height and from 3 to 8 feet in diameter. The lower portion of the walls of these filters are cone shaped and the bottom of each filter is provided with a perforated plate, over which is placed a filter cloth to prevent particles of char from passing out with the clear, purified sugar solution. A door near the bottom of the wall of each filter is provided for the removal of the spent or partially spent charcoal.

The clear, unrefined sugar solution from the mechanical filters⁷⁴ is slowly admitted (at a temperature of approximately 180° F.) through a pipe at the top of each charcoal filter and permitted to percolate down through the column of charcoal. After the charcoal is completely submerged and the air driven out of the granules, the valve controlling the inflow of the raw sugar solution is opened wide and the regular filtration and purification process begins. It should take at least three hours for the sugar solution to pass through the column of charcoal and be discharged from the exit pipe at the base of the filter, since long contact with the charcoal is essential in order to completely decolorize and purify the solution and obtain one from which the maximum amount of sugar can be crystallized.

⁷³ Sugar, p. 116 (1925).

⁷⁴ Ordinary filter presses for the removal of sediment and precipitated material from raw sugar solutions.

The quantity of char required (expressed as a percentage of the dissolved sugar in the raw sugar liquor) to yield first and second grade refined liquors will vary according to the purity and source of the sugar solution. According to Fairrie, solutions which have been properly treated before the charcoal filtration require from 175 to 200 per cent of charcoal to remove their impurities. In other words, 100 tons of sugar require from 175 to 200 tons of animal charcoal for its refinement. Normally such char will remove about 97 per cent of the coloring matter and about 20 per cent of the mineral salts from the sugar solution.

The same authority states that the total quantity of char utilized for liquors and mother liquors expressed as percentage of raw cane sugar entering the refinery varies from 70 to 100 per cent. Fairrie⁷⁵ is careful to state, however, that these figures are only given as a guide since some refiners exceed them, while others use less charcoal.

After being in use from 48 to 60 hours the refining power of the charcoal begins to diminish as is evidenced by the appearance of color in the filtrate. In order to restore the efficiency of the char, therefore, the valve controlling the incoming raw sugar solution is closed and the column of liquid in the filter allowed to descend until the upper part of the charcoal filter is exposed. Boiling water is then admitted which forces the sugar solution before it and dilutes that in the pores of the charcoal granules.

After this operation (which is known as "sweetening off" the charcoal) has been continued for about 16 hours the solution emerging from the base of the filter bed has a concentration of about one per cent of sugar. The water still in the filter is then allowed to stand for some time in order that it may thoroughly impregnate the char, after which the filter is thoroughly washed with boiling water. These final washings are run out into the sewer, since the impurities contained therein are so much higher than the sugar content that it is not practicable to separate and recover the latter.

When the washing is completed (which requires from 12 to 16 hours) the charcoal is allowed to drain, after which the filter is again ready for use.

Fairrie⁷⁶ states that about one ton of water is required to "sweeten off" every ton of charcoal and from one-half to one ton is necessary to wash it.

Eventually the washing, or sweetening off process, will no longer restore the purifying properties of animal charcoal and it is then necessary to reburn the char in order to revivify it.

⁷⁵ Loc. cit., p. 121.

⁷⁶ Sugar, p. 85 (1925).

Revivifying kilns are so constructed that the partially spent charcoal granules are first dried, then heated or reburned at a high temperature and finally cooled in their downward passage through pipes which diminish in diameter from top to bottom. The reburning process opens up the pores of the charcoal and destroys or drives off part of the absorbed impurities, rendering the granules again effective as an absorbing medium.

After long use, however (even where the greatest care has been exercised in washing and revivifying the material), animal charcoal loses its effectiveness and is said to be "spent." Such char is then utilized in the manufacture of phosphoric acid or dissolved bone black for fertilizer purposes.

Most of the sugar refineries still employ animal charcoal rather than activated vegetable carbons in effecting the final purification of their solutions. This may be due in part to the fact that this method of treatment is well understood and the bulk of the refineries are equipped with the necessary apparatus. Fairrie⁷⁷ states, however, that "any refiner contemplating an addition to his animal charcoal filter plant, should carefully consider the use of Norit⁷⁸ in the mechanical or cloth filtration process. In this way he can send partly decolorized liquors to the charcoal house and effect an increase in the decolorizing capacity of his refinery for a smaller expenditure than if he installs new charcoal filters and accessories."

Phosphates in Fermentation Processes and Yeast Culture Media.

Historical.

The processes of fermentation and putrefaction are chemical phenomena which were recognized from earliest times, but their causes remained unknown or unproven until the middle and latter part of the nineteenth century.

In 1837 and 1838 three investigators, Cagniard Latour,⁷⁹ Theodore Schwann,⁸⁰ and Kützing,⁸¹ independently, but almost simultaneously, hit upon the fundamental secret of alcoholic fermentation, arriving at the conclusion through microscopic investigations that the fermentation process is brought about by a living organism and is dependent on the reproduction of the yeast cell.

This view, however, was bitterly opposed at that time by such

⁷⁷ Loc. cit., p. 149

⁷⁸ The trade name for an activated vegetable carbon.

⁷⁹ Ann. Chem. Phys., Vol. 68, pp. 206-222 (1838).

⁸⁰ Ann. Physik., Vol. 41, pp. 184-193 (1837).

⁸¹ J. pr. Chem., Vol. 2, pp. 385-409 (1837).

leading chemists as Berzelius,⁸² Liebig,⁸³ and Wohler,⁸⁴ who regarded yeast as a chemical compound and would not admit the value of the microscopic evidence showing that it was a living plant capable of sustaining itself and of rapid reproduction in nutrient solutions. These authorities held that the phenomenon of fermentation was caused either by the instability of the so-called compound of yeast which communicated this unstable condition to the sugar solution, or to a catalytic power exerted by the yeast compound.

It was the classical work of Pasteur⁸⁵ which definitely established the origin and functions of yeast and convinced the scientific world that fermentation changes were due to specific organisms which produced them in the exercise of their vital functions.

While Buchner⁸⁶ later succeeded in obtaining from yeast a liquid (containing zymase) which in the absence of living cells was capable of decomposing sugar into carbon dioxide and alcohol, this fermenting agent, as far as we know to-day, is the product of a life process and can be produced in no other way.

Nature and Culture of Yeast.

Yeast belongs to a group of so-called organized ferments and consists of microscopic cells, round or oval in form, which usually multiply by the process of budding. These buds become divided from the parent cell by a membrane, but frequently remain adherent after giving rise to further buds so that a kind of chain of succeeding generations is produced. The most favorable temperature for the growth and reproduction of the yeast cells is from 25° to 30° C., the upper limit at which growth ceases being about 53° C. and the lower limit being a few degrees above the freezing point.

Just as in the case of animals and the higher types of plant life, phosphorus in the form of orthophosphate plays an essential rôle in the growth and propagation of yeast and hence is an important constituent of yeast culture media.

While yeast consists chiefly of carbon, hydrogen, oxygen and nitrogen, its mineral content is quite appreciable and according to the investigations of Mayer,⁸⁷ which were later confirmed by Elion⁸⁸ and Stern,⁸⁹ the proportions of the various inorganic ingredients (including

⁸² Berz. Jahresberichte, Vol. 18, pp. 400-403 (1839).

⁸³ Annalen, Vol. 30, pp. 250-287 (1839).

⁸⁴ Annalen, Vol. 29, pp. 100-104 (1839).

⁸⁵ Ann. Chim. Phys. (3), Vol. 58, pp. 323-426 (1860); Compt. rend., Vol. 80, p. 452 (1875).

⁸⁶ Berichte, Vol. 30, pp. 117-124 (1897).

⁸⁷ Lehrbuch der Gärungschemie (1902), 5th Edition.

⁸⁸ Studien über Hefe, Cent. Bakt. 14 (1893).

⁸⁹ Nutrition de la levure, Jour. Chem. Soc., 1899 and 1901.

phosphates) in a culture medium best suited for the propagation of yeast are the same as those present in the yeast as shown by analysis.

In the following analyses (as reported by Mitscherlich⁹⁰) it will be seen that P_2O_5 is the predominating mineral constituent of the ash of the yeast plant. Potash, magnesia and sulfur, however, are also indispensable to the life of yeasts.

TABLE LXIII
ANALYSES OF THE ASH OF YLASE (PER CENT)

Ingredient	Upper Fermentation Yeast	Lower Fermentation Yeast
Potash (KO_2)	38.8	28.3
Lime (CaO)	1.0	4.3
Magnesia (MgO)	6.0	8.1
Phosphoric acid (P_2O_5)	53.9	59.4
Silica (SiO_2)	trace

As far back as 1860 Pasteur⁹¹ produced a crop of yeast in a liquid medium containing only comparatively simple substances of known composition, such as sugar, ammonium tartrate and a mineral phosphate. This is possibly the first experiment recorded wherein an inorganic phosphate was purposely added to a culture medium and it seems doubtful if Pasteur knew at that time what a significant rôle phosphorus plays in the growth and reproduction of the yeast cell.

Wroblewski⁹² in 1901 observed that the presence of sodium phosphate increased the fermentation of yeast juice, and Buchner, who also noted the same phenomenon, attributed it to the alkalinity of this phosphate compound.

The important part which phosphates play in yeast culture media was discovered in seeking the cause of the rapidly diminishing fermenting power of yeast juice. With the idea of producing anti-ferments, the fermentation process was conducted in the presence of serum from animals into which yeast juice had been injected. It was observed that instead of inhibiting the fermentation of yeast juice the presence of serum from both treated and untreated animals increased the rate of fermentation.

Autolyzed yeast juice which had been boiled and filtered was also found to produce a marked increase in the fermentation of sugar solutions.

⁹⁰ *Lehrbuch d. Chem.*, Vol. 1, p. 370 (1884).

⁹¹ *Ann. Chim. Phys.* (3), Vol. 58, pp. 323-426 (1860).

⁹² *Ber.*, Vol. 31, pp. 3218-3225; *Centr. Physiol.*, Vol. 12, pp. 697-701 (1898)

According to Harden and Young,⁹³ the increase in fermentation of such solutions was finally traced to the two following causes: (1) the presence of phosphates in the liquid, and (2) the existence in boiled fresh yeast juice of a co-ferment, the presence of which is indispensable for fermentation.

It has now been pretty generally conceded that for the rapid decomposition of sugar solutions by fermentation, the presence of a phosphate is highly important if not essential. This phosphate is not only in the yeast juice but as shown in Table LXIII, is a constituent part of the cell.

Harden⁹⁴ states that the phosphorus takes a very active part in the fermentation and goes through a remarkable cycle of changes, the decomposition of the sugar being accompanied by the formation of a complex hexosephosphate from which the phosphate is split off and again rendered available by means of a special enzyme termed hexophosphatase.

Action of Phosphates in Fermenting Mixtures.

When a suitable quantity of a soluble phosphate is added to a fermenting solution of a sugar and yeast juice the rate of fermentation rapidly increases. The speed of the reaction being sometimes as much as 20 times that at which it normally proceeds.

This increase in the rate of fermentation continues for a while and then gradually falls to a point approximately equal to the original rate.

Harden and Young,⁹⁵ after careful experimentation, found that during this period of enhanced fermentation the amount of carbon dioxide and alcohol produced exceeded those formed in the absence of added phosphate by a quantity exactly equivalent to the phosphate added in the ratio of CO_2 or $\text{C}_2\text{H}_5\text{OH}:\text{Na}_2\text{HPO}_4$. It is not within the scope of the present work to give in detail the manner in which these experiments were conducted but the results obtained indicated that a definite chemical reaction occurs in which both sugar and phosphate are concerned. This conclusion was confirmed by other experiments in which the solutions employed were boiled and filtered (after the rate of fermentation had subsided) and it was found that nearly all of the phosphate was in organic combination.

Bermann and Kulp⁹⁶ made periodic determinations of the inorganic phosphate present during the fermentation of a nutrient solution of molasses containing small quantities of superphosphate and ammonium

⁹³ J. Physiol., Vol. 32, proceedings of Nov. 12 (1904); Proc. Chem. Soc., Vol. 21, pp. 189-191 (1905).

⁹⁴ Alcoholic Fermentation, p. 17 (1914).

⁹⁵ The Alcoholic Fermentation of Yeast Juice, J. Physiol., Vol. 32, Proceedings of Nov. 12 (1906).

⁹⁶ Wochschr. Brau., Vol. 42, p. 39-40 (1925).

sulfate and found that rapid esterification of the P_2O_5 with the sugars takes place during the early stages of fermentation. These same investigators in another article⁹⁷ state that the yeast cell consumes phosphate in an irregular manner but that the rate of consumption gradually falls off with time.

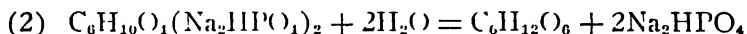
Euler and Johansen⁹⁸ claim that in their experiments where equivalent quantities of glucose and a phosphate were present in a fermenting mixture, all of the glucose had disappeared when the phosphate was completely esterized.

Harden⁹⁹ expresses the reaction between glucose and a dibasic phosphate salt as follows:



According to the above equation one molecule of the sugar is converted into carbon dioxide and alcohol while the other molecule is converted into a hexosephosphate and water.

When alcoholic fermentation ceases, however, there is a marked and rapid increase in the quantity of free or mineral phosphate since the hexosephosphate undergoes hydrolysis thus—



In other words, reversion takes place and glucose and water are again produced. But since the quantity of glucose (or other sugar) thus formed is equivalent only to the mineral phosphate in the solution the reaction cannot again proceed according to equation (1) until further quantities of sugar are added.

If an excess of sugar be present, then the decomposition of the hexosephosphate (as alcoholic fermentation slackens) gives free mineral phosphate to react with further quantities of glucose but the reaction then proceeds at only a slow or normal rate.

Harden and Young¹⁰⁰ found that by the simple expedient of renewing the supply of mineral phosphate (in sugar solutions) as fast as it was converted into hexosephosphate, a high rate of fermentation could be maintained for a considerable period of time.

Thorp¹⁰¹ suggests the following scheme as explaining the action of sugar and phosphate in the yeast cell.

"The sugar first diffuses into the cell and it has been shown that

⁹⁷ Chem. Listy, Vol. 19, pp. 79-82 (1925).

⁹⁸ Zeitsch. Physiol. Chem., Vol. 85, pp. 192-208 (1913).

⁹⁹ Loc. cit.

¹⁰⁰ Loc. cit.

¹⁰¹ Dictionary of Applied Chemistry, Vol. 2, p. 522 (1912).

the rate of diffusion is much more than sufficient to supply the sugar necessary for fermentation. . . . Inside the cell the sugar, either as such or having undergone some change, combines with the fermenting complex and is thereby brought into relation with phosphate probably also combined with the fermenting complex. This association of fermenting complex, sugar and phosphate then breaks down with the liberation of the fermenting complex accompanied either by the formation of carbon dioxide, alcohol and hexosephosphate, as in equation (1), or of the products of some intermediate stage of this reaction. It is probably the rate of this decomposition which is measured as the rate of fermentation."

With few exceptions all of the yeasts isolated up to the present grow well in artificial media containing inorganic phosphate salts. In the following table compiled from data presented by A. Guilliermond and F. W. Tanner¹⁰² some of the common culture media recommended by various authorities are given:

TABLE LXIV
COMMON YEAST CULTURE MEDIA CONTAINING INORGANIC SALTS OF ORTHOPHOSPHORIC ACID

Authority	Quantities of Ingredients (Grams)								
	Peptone	Maltose	Sugar	Asparagin	Magnesium Sulfate	Ammonium Sulfate	Potassium Phosphate	Calcium Phosphate	Distilled Water
Hansen's medium									
No. 1	1	5	0.2	...	0.3	...	100
Hansen's medium									
No. 2	1	5	0.5	...	0.3	...	100
Mayer's culture medium	15.0	...	5.0	0.75	5.0	0.5	1000
Laurent's medium	any sugar	...	0.1	4.71	0.75	...	1000
Haydruck's medium	100	2.5	17.0	...	50.0 ^a	...	2000
Colin's solution	20	...	1.0	2.0 ^b	2.0 ^c	0.1	200

^a Potass. acid phosphate (KH_2PO_4).

^b Ammonium tartrate instead of ammonium sulfate.

^c Dicalcium phosphate (CaHPO_4).

In the above table potassium phosphate is the chief carrier of phosphoric acid specified, but disodium phosphate and mono- and dicalcium phosphates are also employed. In recent years ammonium phosphate as an ingredient of yeast culture media has grown in favor since this

¹⁰² The Yeasts, 424 pages (1920).

compound furnishes both the P_2O_5 and nitrogen required in the growth and propagation of the yeast cells.

A number of patents have been issued in which ammonium phosphate is mentioned as the chief carrier of nitrogen and phosphoric acid in yeast culture processes.¹⁰³

L. E. Buffington¹⁰⁴ claims to have developed a "no fermentation period dough" (containing ammonium phosphate) with which the entire bread making operation may be completed in less than two hours.

According to this invention small quantities of pepsin, lactic acid and ammonium phosphate are mixed with the usual bread making ingredients and the dough baked almost immediately rather than allowing it to stand for several hours as is done in the case of ordinary bread made with yeast.

Phosphates in the Weighting of Silk.

Before being manufactured into textiles, raw silk is subjected to several treatments with a view to making it soft and glossy and rendering it suitable for subsequent dyeing operations.

The first step in processing the fiber is called discharging, stripping or degumming, and is really a scouring process designed to remove the sericine or silk glue which causes the fiber to feel coarse and stiff.

This sericine is dissolved by treating the silk with a soap solution at a temperature just a little below the boiling point (205° F.). In this scouring process the silk loses from 20 to 30 per cent in weight, but the product is soft and lustrous and in an excellent condition for the next step in its treatment. The soap solution which becomes heavily charged with the gum-like material (originally a part of the silk fiber) is subsequently utilized in the dyeing process, a discussion of which is not within the scope of this book.

After being scoured and washed free of soap, the silk is ready for weighting, which adds to the fiber a quantity of material sometimes more than equal to that lost by the scouring process.

The details of silk weighting were at one time jealously guarded and while the processes employed are now no longer secret, little is known of how and when they were discovered and developed.

The most important agent in the weighting of silk is tin, the salts of which are more readily absorbed by the silk fiber than those of any other metal. Tin chloride is usually employed for this purpose, although tin sulfite is said to be in some respects superior to the chloride.

¹⁰³ U. S. Patents Nos. 1,449,103 (1923); 1,449,111 (1923); 1,449,127 (1923); 1,580,550 (1926).

¹⁰⁴ U. S. Patent 1,500,545 (1924).

The affinity of silk for tin is such that it will readily take up from 8 to 10 per cent of its weight of this oxide and in some types of goods the weight of the silk is more than doubled.

Proper tin weighting has a most beneficial effect on both the luster and handling of the silk and if used in connection with phosphates does little or no harm to the strength, elasticity, and durability of the finished goods.

The discovery of the value of disodium phosphate in the weighting process was a great advance in the art of silk manufacture. Before the advent of phosphates, the goods after being treated with a salt of tin were immersed in or washed with ammonia water, sodium carbonate, or some other alkali solution, for unless the slight acidity of the tin salt was neutralized, the fiber was unable to be weighted any further by repeated treatments with a tin solution. After neutralization, however, the fiber which acts like a free base is able to take up an additional quantity of the tin salt.

The treatment of the silk with dilute alkali always left a precipitate of hydrated tin oxide on the fiber and this free base often proved injurious to the goods when they were exposed to air and light.

By the use of disodium phosphate in lieu of the alkalies mentioned above, the acidity of the tin chloride is neutralized and a phosphate of tin produced with the result that the durability and strength of the fiber is increased instead of diminished and the cost of weighting considerably reduced.

It has subsequently been shown that the use of sodium silicate, in addition to a tin salt and disodium phosphate makes it possible to increase even further the percentage of tin absorbed by the silk fiber.

Silk weighted with tin phosphate is perfectly suitable for dyeing; in fact, according to Matthews,¹⁰⁵ modern silk dyeing is economically impossible without tin weighting and the use of phosphates has rendered the weighting process both safe and profitable.

"Manufacture and Uses of Tricalcium Phosphate."

Relatively small quantities of tricalcium phosphate have been used for some time in the production of certain tooth pastes and in medicinal preparations, where a bone building material is prescribed.

In recent years, however, a new and wider use for pure tricalcium phosphate has been developed which has made the production of this compound of some commercial importance. This is the employment of tricalcium phosphate as a conditioner in table salt.

Practically all table salt contains impurities sufficient to render it

¹⁰⁵ The Textile Fibers, 1053 pages, John Wiley and Sons, Inc. (1924).

somewhat hygroscopic, particularly in certain climates and during seasons when the humidity is high.

This hygroscopic property of salt causes it to cake and at times become so damp that it is inconvenient to handle and difficult to distribute uniformly in the food which it is desired to season.

It has been found by mixing 1 per cent or more of certain light flocculent precipitated compounds with such salt that the latter largely loses its caking properties and will flow sufficiently freely to permit its ready distribution in food products.

The probable action of these finely divided insoluble precipitates is to coat the salt grains with a thin film which not only protects them from the humidity of the air but also acts as a kind of dry lubricant, preventing the salt particles from adhering to one another.

The two precipitated compounds which have given the greatest satisfaction in imparting that desirable "free running" property to table salt, are magnesium carbonate and tricalcium phosphate, but the use of the latter compound has recently grown in favor, it being argued that the presence of small percentages of inorganic phosphates in food products is unobjectionable if not actually desirable.

Since tricalcium phosphate is generally regarded as the end product representing the complete neutralization of phosphoric acid by lime, its manufacture would appear off hand to be a relatively simple process.¹⁰⁶ In actual practise, however, considerable difficulty may be experienced in obtaining a product free from either dicalcium phosphate or hydrated lime unless great care be exercised in its preparation and strict attention given to the various manufacturing details. The general procedure employed may be briefly described as follows.

An emulsion of milk of lime is first prepared, and to insure the absence of small lumps of burned lime or of undesirable impurities this emulsion is strained, diluted and mixed with dilute phosphoric acid. In order to insure the absence of free lime in the product, the quantity of phosphoric acid employed is slightly less than that theoretically required to produce tricalcium phosphate.

The mixture is heated and agitated in large tanks until sufficient time has elapsed for the reaction to go to completion. The thin emulsion of tricalcium phosphate is then pumped to a filter press and the bulk of the water eliminated, after which the damp cake is removed and dried at a temperature sufficiently low to prevent the loss of the one molecule of water of crystallization, which such tricalcium phosphate contains.

¹⁰⁶ Some doubt exists as to whether or not tricalcium phosphate is actually the final product of the complete neutralization of H_3PO_4 with CaO . A product is often obtained which more nearly conforms to the formula $Ca_2(PO_4)_2CaO$.

The dried phosphate must be milled to obtain a product of the desired degree of fineness, but this operation is relatively simple since it merely consists in breaking up the loose aggregates and is not strictly a grinding process.

The material is then put up in barrels or kegs for the market.

The product prepared according to the general method outlined above will usually contain a small percentage of dicalcium phosphate, but since the conditioning properties of this compound are similar to those of tricalcium phosphate its presence is in no wise objectionable.

No accurate figures are available showing the quantity of tricalcium phosphate annually consumed in tooth paste, medicinal preparations and for conditioning table salt but it appears conservative to estimate this amount at approximately 1,000,000 pounds or 500 short tons.

APPENDIX

TABLE LXV.—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES BY SULPHURIC ACID TREATMENT.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
16,882	1857	Reid, L.	Bone dust, H_2SO_4 , liquid manure, absorbents.	The various ingredients are thoroughly mixed with sulphuric acid and allowed to cure.	Production of phosphate nitrogenous fertilizer.
34,825	1862	Gallicher, J. M.	Bone black (100), H_2SO_4 (46), liquid animal matter (9).	The various ingredients are thoroughly mixed and allowed to cure.	Production of concentrated manure.
38,040	1863	Gale, L. D.	Phosphate guano, animal matter, H_2SO_4 .	Do.	To improve or enrich guano.
41,428	1864	Harper, L.	Guano, liquid animal matter, H_2SO_4 , alkaline salts.	Part of guano is mixed with liquid animal matter, part with H_2SO_4 , alkaline salts are added, and the whole is thoroughly mixed.	To restore guano.
41,663	1864	Hayes, A. A.	Guano, NaCl, H_2SO_4 , animal matter.	Ingredients are thoroughly mixed and allowed to cure.	To separate and treat guano.
42,006	1864	Liebig, G. A.	Navassa guano, H_2SO_4 .	The coarse particles of guano are separated from the fine and each part treated separately with H_2SO_4 .	The production of dry pulverulent product.
46,700	1865	Potts, R. B.	Do.	The guano is sprinkled with H_2SO_4 .	Improved product due to efficient mixing.
59,978	1866	Figaniér, A. de.	Phosphate rock, H_2SO_4 .	Phosphate rock and H_2SO_4 are mixed in a special machine.	To produce pulverulent acid phosphate.
75,271 } 75,272 } 75,325 }	1868 1868 1868	Horsford, E. N. Wilson, Geo. F.	{ Tribasic phosphate of lime, HNO_3 , H_2SO_4 . Bone or its derivatives, nitric acid or salt cake, water, steam.	$Ca_3(PO_4)_2$ is dissolved in HNO_3 . H_2SO_4 is added and $CaSO_4$ thus precipitated. HNO_3 is driven off by heat. Bones, water, and hot nitric cake, salt cake, or both, are placed in a revolving cylinder, and steam is led into the mixture under high pressure.	Production of fertilizer material and distillation of HNO_3 or HCl.
75,327	1868	Do.	Bones, steam, water, H_2SO_4 , bone charcoal.	Diluted sulphuric acid is first heated in a lead-lined vat, heated by a steam coil, bones and bone charcoal are then added.	Production of $CaSO_4$, $CaH_4(PO_4)_2$, and $(NH_4)_2H(PO_4)$.
75,336	1868	Wilson, G. F., and Horsford, E. N.	$CaH_4(PO_4)_2$, H_2SO_4 , burned bone.	Ingredients are mixed and product is leached.	Production of acid phosphate.
75,338 75,339	1868 1868	Do. Do.	Bones, H_2SO_4 . Phosphate rock, HCl or HNO_3 , purified H_2SO_4 .	H_2SO_4 is purified and then added to solution of phosphate, dissolved in HNO_3 . H_2SO_4 is added to solution of bones in HNO_3 .	Do. Production of pure acid phosphate.
76,763 86,289	1868 1869	Horsford, E. N. Duvall, A.	HNO_3 , H_2SO_4 , bones. Phosphate rock, steam, H_2SO_4 .	Phosphate rock and H_2SO_4 are mixed by means of steam or by air blast.	Do. Improved method of mixing acid and rock.
90,367	1869	Lalor, Wm.	H_2SO_4 from refining of petroleum phosphate rock.	Ingredients are thoroughly mixed and product is allowed to cure.	Utilization of waste acid and production of acid phosphate.
113,416	1871	Fortes and Paston.	Sewage, phosphate rock, H_2SO_4 , $CaCO_3$.	Phosphate rock is acidulated and product treated with sewage.	Improvement in treatment of sewage and production of fertilizer.
125,613	1872	Pratt, N. A.	Phosphate rock, slaked lime, H_2SO_4 .	Phosphate rock is acidulated and then passed through filter press. Filtrate is then mixed with slaked lime.	Production of two cakes of fertilizer.
126,904	1872	Do.	Phosphate rock, H_2SO_4 , lime.	H_2SO_4 is mixed with phosphate rock while grinding the latter. Bags are filled with product and pressed lime is added to material coming through bags.	Improvement in treating phosphate rock.

TABLE LXV.—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES BY SULPHURIC ACID TREATMENT—Continued.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
128,752	1872	Ratt and Lewis.....	Phosphate rock, H_2SO_4 .	H_2SO_4 is mixed with phosphate rock while grinding the latter. Bags are filled with product and soluble P_2O_5 pressed out. Fertilizer salts are added to extract and whole evaporated.	Production of fertilizer and method of making same.
130,298	1872	Horsford, E. N.....	Burned bones, H_2SO_4 , water, bone coal, HCl , heat, air, starch.	Burned bones are treated in two charges, the first with H_2SO_4 and the second with HCl . The solutions resulting are mixed and evaporated and taken up with starch.	Production of acid phosphate and absorption of same.
137,635	1873	Storck, H., and Lyte, F. M.....	Phosphate rock, H_2SO_4 , $Ba(OH)_2$ or other convenient form of barium.	Phosphate rock is converted into H_3PO_4 by H_2SO_4 . Solution is drawn off and treated with $Ba(OH)_2$. This is filtered and the solution used to produce any desired phosphate.	Production of H_3PO_4 or phosphates free from lime and sulphates.
173,621	1876	Gruftit, A. G.....	Bone dust, guano, manure, H_2SO_4 .	Ingredients are thoroughly mixed and allowed to cure.	Improved fertilizer.
211,238 238,240	1879 1881	Juganston, Jonas Lippincott and Lippincott	Ground bone, H_2SO_4 , CaO .	Ingredients mixed and allowed to cure.	Production of available P_2O_5 .
276,143	1883	Knight, J. J.....	Slag (blast furnace), H_2SO_4 .	The blast furnace slag is thoroughly sprinkled with H_2SO_4 .	Production of phosphate fertilizer.
278,383	1883	Young, J. K.....	Phosphates of iron and aluminum, H_2SO_4 .	Ingredients are thoroughly mixed and acid extract filtered.	Production of H_3PO_4 .
278,480 281,655	1883 1883	Do..... Koefoed, A. H.....	H_2SO_4 , night soil, H_2SO_4 , iron or aluminum phosphate, lime or dolomite, acid.	Ingredients are ground, mixed, calcined, and treated with a mineral acid (H_2SO_4 , HNO_3 , or HCl).	Production of improved fertilizer.
301,248	1884	Liebig, G., and Gibbons, J. F.....	Phosphates containing iron or aluminum, or both, dilute H_2SO_4 .	Do. The phosphates and acid are thoroughly mixed and the resulting solution heated.	Production of soluble P_2O_5 .
302,666	1884	Do.....	Phosphates of iron or aluminum, dilute H_2SO_4 , other salts.	The phosphates and acid are thoroughly mixed, the solution filtered, dried, and other fertilizer salts are added.	Production of soluble P_2O_5 .
305,249	1884	Stillman and Koefoed.....	Iron and aluminum phosphates, dolomite, H_2SO_4 .	The phosphates and dolomite are mixed and calcined, then treated with H_2SO_4 .	Production of dry fertilizer containing P_2O_5 and other fertilizer elements.
322,698	1885	Dibben and Dubbs.....	Solution of $HNaSO_4$, phosphate rock.	The $NaHSO_4$ is dissolved in hot water and the solution used to decompose phosphate rock.	Production of phosphate which does not readily revert.
407,240	1889	Powter, N.....	Redonda phosphates, animal matter, H_2SO_4 .	Ingredients are thoroughly mixed and allowed to cure.	Production of soluble phosphate.
407,241	1889	Do.....	Guano, animal matter, H_2SO_4 , $CaCO_3$.	Ingredients are mixed thoroughly and allowed to cure.	Production of improved fertilizer.
418,259	1889	Winsinger, C. E. D.	Phosphate of lime, H_2SO_4 , Na_2SO_4 , lime, heat.	Acid phosphate or H_3PO_4 is produced by the action of H_2SO_4 on $Ca_3(PO_4)_2$. The solution is treated with Na_2SO_4 , giving NaH_2PO_4 . Addition of Na_2CO_3 gives $NaHPO_4$, and precipitates iron and alumina, which is filtered off. Milk of lime is then added to the solution and the whole filtered.	Production of precipitated phosphates of iron alumina, caustic soda, and precipitated lime phosphate.

TABLE LXV.—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES BY SULPHURIC ACID TREATMENT—Continued.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
445,255	1891	Seal, Wm. B.	Phosphate rock, H_2SO_4 , coal dust, animal matter.	Ingredients are thoroughly mixed and allowed to cool.	Production of improved fertilizer.
445,567	1891	Memminger, A.	Phosphate rock, CaF_2 , H_2SO_4 .	Phosphate rock and CaF_2 are ground intimately together with H_2SO_4 .	Production of dry acid phosphate.
459,575	1891	Glaser, Chas.	Phosphate material, dilute H_2SO_4 .	Phosphate material mixed with dilute H_2SO_4 . Solution of H_2PO_4 resulting is used to dilute more H_2SO_4 , and the mixture of acid is used to treat more phosphate rock.	Production of H_3PO_4 of growing strength without evaporation.
494,940	1893	Rissmuller, Ludwig.	Phosphate rock or bones, organic matter, H_2SO_4 .	Organic matter is dissolved in H_2SO_4 , fat is skimmed off, and phosphate rock or bones added.	Production of improved fertilizer.
496,687	1893	Hoffman, P. C.	Phosphate rock, H_2SO_4 , external heat.	Ingredients mixed in the usual way and heated.	Rapid production of soluble phosphate.
515,708	1894	Gregory, John	Bone black from oil purification, H_2SO_4 .	Ingredients thoroughly mixed and boiled. Grease is skimmed off.	Production of phosphatic fertilizer from spent bone black.
629,996	1899	Holtmann, J.	Apparatus for making phosphoric acid.	Phosphate rock and H_2SO_4 are fed into two agitators in series and then to centrifugal machine where acid is separated. It is then run into several concentrators and a cooler.	Apparatus for making phosphoric acid.
655,458	1900	Saxl, H.	Phosphatic material, H_2SO_4 , H_2O .	Phosphate is thoroughly mixed with acid and allowed to stand; product is then mixed with water and solution decanted. Solution is then used to treat more phosphate.	Production of concentrated phosphate.
657,717	1900	Wharton, J. C.	Phosphate rock, NH_4Cl , H_2SO_4 , CO_2 , lime, heat, water.	$(NH_4)_2SO_4$ and HCl are first produced by treating NH_4Cl with H_2SO_4 . The evolved HCl is led into a mass of phosphate rock suspended in water. Phosphate solution is then filtered and evaporated and placed in a closed container into which NH_3 is led from the decomposition of $(NH_4)_2SO_4$ by lime. The lime phosphate is thus precipitated and filtered off. The solution is then treated with CO_2 which precipitates the lime and regenerates NH_4Cl . Garbage is treated with phosphate rock at $400^\circ F$. Phosphate rock is then thoroughly mixed with product.	Production or separation of precipitated lime phosphate.
683,014	1901	Augstadt and Cleaver	Phosphate rock, garbage, H_2SO_4 .	Phosphate rock is mixed with H_2O and sufficient H_2SO_4 to attack carbonates and fluorides in rock. $NaHSO_4$ is then added and the water removed by evaporation.	Production of improved fertilizer.
690,049	1901	Cheeseman, Lewis	Phosphate rock, $NaHSO_4$.	Garbage is first digested to free it from grease, then mixed with phosphate rock and H_2SO_4 .	Production of a mixture of monocalcium and dicalcium phosphates.
703,295	1902	Newport, R. B.	Phosphate rock, garbage, H_2SO_4 .	Sufficient H_2SO_4 is added to convert phosphate rock to dicalcium phosphate.	Production of improved fertilizer.
736,730	1903	Hoyermann, G.	Phosphate rock (100), H_2SO_4 (30).	Phosphate rock and niter cake are digested with water. The liquor is then filtered and mixed with carbon.	Production of trisodium phosphate.
744,128	1903	Strickler, E. H.	Phosphate rock, niter cake, carbonaceous matter.	Phosphate rock is dissolved in cold H_2SO_4 . The free SO_2 is then eliminated by boiling and a mixture of $CaHPO_4$ and $CaSO_3$ is precipitated. After separation, H_2SO_4 or some other acid is added to the ppt.	Production of $CaHPO_4$ free from sulphites.
852,372	1907	Bergmann, E.	Phosphate rock, water, SO_2 and Fe_2O_3 , HCl , or H_2SO_4 .		

TABLE LXV.—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES BY SULPHURIC ACID TREATMENT—Continued.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
997,968	1911	Cusatelli, G.	Phosphate rock, H_2SO_4 , HNO_3 .	Phosphate rock is treated in the usual manner with H_2SO_4 to which a small quantity of HNO_3 is added.	Production of rich phosphate fertilizer which does not readily revert.
1,003,681	1911	Williams, R.	Phosphate rock, H_2SO_4 , refrigeration, NH_3 .	Phosphate rock is mixed with H_2SO_4 at low temperatures so that iron and aluminum compounds are unattacked.	Economy in H_2SO_4 and production of soluble P_2O_5 .
1,020,153	1912	Newberry, S. B., and Barrett, H. N.	Phosphate rock, H_2SO_4 , HCl, heat.	Phosphate rock is treated with H_2SO_4 and HCl. The solution is filtered from the $CaSO_4$ and evaporated to dryness. HCl is evolved and used again.	Production of $CaHPO_4$.
1,083,429	1914	Brunswick, F.	Phosphate material, acid.	Treat material with less dil. sulphuric acid (or acid stronger than phosphoric) than is required for the calcium of phosphate and stopping reaction before impurities go into sol. Separate liquid and treat with additional acid, then take up excess acid with bone black.	Production of phosphoric acid.
1,105,304	1914	Réed, E. W.	Phosphate rock (finely ground), H_2SO_4 .	Phosphate material is thoroughly agitated by means of an air current and simultaneously sprayed with H_2SO_4 .	Production of acid phosphate.
1,137,531	1915	Pratt, G. L.	Phosphate, H_2SO_4 , special acid phosphate machinery.	Phosphate dust mixed with acid is delivered to special system of curing dens.	Production of acid phosphate.
1,168,255	1916	Herzka, E.	Molasses refuse, phosphate material, H_2SO_4 , SO_2 and O_2 gases.	Molasses residue is concentrated, mixed with ground phosphate and the mixture treated with H_2SO_4 . Moistened ground phosphate material is subjected to the action of SO_2 and SO_3 gases in presence of oxygen.	Production of a potash, nitrogen and phosphate fertilizer.
1,246,636	1917	Meyers, H. H.	Phosphate material, acid hydrocarbon sludge, heat.	Phosphate material is treated with an acid hydrocarbon sludge containing enough H_2SO_4 to convert phosphoric matter to phosphoric acid. Heat until all of volatile matter is driven off. Treat the residue with a calcareous phosphate in presence of water.	Production of superphosphate containing gypsum, and finely divided carbon.
1,255,829	1918	Blumenberg, H., Jr.	Phosphate rock, H_2SO_4 , alkali sulphate, HCl.	Phosphate rock is treated with H_2SO_4 sufficient to form dicalcium phosphate. The dicalcium phosphate is treated with a solution of alkali sulphate and filtered. The filtrate containing dialkali phosphate and alkali sulphate is again treated with a fresh portion of dicalcium phosphate and filtered. Alkali sulphate is separated from filtrate by concentration and salting out. The remaining solution is evaporated to form crystals. These crystals are dried and treated with HCl and the salt separates. The H_2PO_4 solution remaining is treated with fresh phosphate rock.	Production double superphosphate.
1,351,672	1920	Meigs, C. C.	Phosphate rock, H_2SO_4 , alkali sulphate, HCl.	Wet precipitated dicalcium phosphate is dried after adding H_2SO_4 to prevent dusting.	Production of a non-dusting phosphate fertilizer.
1,375,115	1921	Shoeld, M.	Precipitated phosphate, H_2SO_4 .	Ground phosphate rock is mixed with H_2SO_4 and delivered to den where reaction takes place. Pulverize and add phosphate dust to take up excess acid.	Process for making acid and superphosphate.
1,383,912	1921	Doyle, W. T.	Phosphate rock, H_2SO_4 , acid phosphate apparatus.		

TABLE LXV.—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES BY SULPHURIC ACID TREATMENT—Continued.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
1,413,048	1922	Matheson, A.	Alunite, phosphate material, heat.	Alunite is roasted in furnace to 700 to 900° C. and sulfur fumes driven off are passed through phosphate material in the presence of water forming H_2SO_4 which reacts with phosphate rock.	Production of superphosphate.
1,459,124	1923	Webster, H. A.	Phosphate rock, sulphuric acid, water, heat.	1000 lbs. phosphate rock (60 B.P.L.) is suspended in 1000 lbs. of water and 600 lbs. 60° B ϵ . H_2SO_4 diluted with 1000 lbs. water are added. After "setting" it is treated with 1000 lbs. additional water and heated to 80° C. The water soluble P_2O_5 is decanted off and the residue dried.	Production of superphosphate.
1,461,077	1923	Do.....	Low-grade phosphate rock (200 mesh), (100 parts), sulphuric acid (75 parts), (52° B ϵ).	Finely ground phosphate rock and sulphuric acid are fed simultaneously into a mixer and intimately mixed and later aerated. It is claimed that the resultant product is high in di-calcic phosphate.	Production of superphosphates from low-grade phosphate rock.
1,483,406	1924	Meyers, H. H.	Phosphate rock, 60° B ϵ , sulphuric acid, water, rotary dryer.	Phosphate rock ground with 30 to 40 per cent of its weight of water, is mixed directly with 60° B ϵ . sulphuric acid and this mixture fed continuously to a rotary dryer where the moisture is reduced to 10%.	Production of acid phosphate.
1,546,946	1925	Singleton, Gray	Phosphate rock, rotary kiln, and sulphuric acid.	Phosphate rock is heated in a rotary kiln with only sufficient temperature to destroy the organic matter without decomposing the carbonates. This rock is then treated with sulphuric acid to produce acid phosphate.	Treatment of phosphate rock for manufacturing acid phosphate.

TABLE LXVI.—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES BY TREATMENT WITH ACIDS OTHER THAN SULPHURIC.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
40,831	1865	Liebig, G. A.	Navassa guano, HCl or SO_2	Either HCl or a solution of SO_2 is substituted for H_2SO_4 in the making of acid phosphate.	To use some other mineral acid.
75,271 } 75,272 } 75,339 }	1868	Horsford, E. N.	{ Tribasic phosphate of lime, HNO ₃ , H ₂ SO ₄ .	$\text{Ca}_3(\text{PO}_4)_2$ is dissolved in HNO ₃ . H ₂ SO ₄ is added and CaSO_4 thus precipitated. HNO ₃ is driven off by heat.	To produce pulverulent acid phosphate.
	1868	Wilson, G. F., and Horsford, E. N.	Phosphate rock, HCl or HNO ₃ purified H ₂ SO ₄ .	H ₂ SO ₄ is purified and then added to solution of phosphate dissolved in HNO ₃ .	Production of pure acid phosphate.
76,763 130,298	1868 1872	Horsford, E. N. Do.	HNO ₃ , H ₂ SO ₄ , bones. Burned bones, H ₂ SO ₄ , water, bone, coal HCl, heat, air, starch.	H ₂ SO ₄ is added to solution of bones in HNO ₃ . Burned bones are treated in two charges, the first with H ₂ SO ₄ and the second with HCl. The solutions resulting are mixed and evaporated and taken up with starch.	Production of acid phosphate and absorption of same.
140,559	1873	Tanner, Benj.	Phosphate rock, H ₂ PO ₄ , lime.	Phosphate rock is treated with water saturated with CO_2 .	Production of acid phosphate of lime.
164,457	1875	Jas. A.	Phosphate rock, CO_2 , water.	Phosphate rock is dissolved by SO_2 under pressure, sulphate of lime separated, and SO_2 driven off from solution by heat. Resulting acid phosphate can be treated as desired.	Production of acid phosphate and drying same with plaster of paris.
196,881	1877	Designolle, G. L. G.	Phosphate rock, SO_2 (under pressure), plaster of paris, heat.	Slack is first treated, then treated with HCl. Milk of lime is then added to the solution.	Production of precipitate containing available P_2O_5 .
279,445	1883	Schriber, Carl	Basic slag, HCl, lime.	Ingredients are ground, mixed, calcined, and treated with a mineral acid (H_2SO_4 , HNO ₃ , or HCl).	Production of soluble P_2O_5 .
281,635	1883	Koefoed, A. H.	Iron or aluminum phosphate, lime or dolomite, acid.	Steam and SO_2 are passed through the heated pulverized phosphate.	Production of available P_2O_5 .
283,427	1883	Scribner, E. A.	Iron or aluminum phosphate, SO_2 , steam.	Phosphate rock is dissolved in H_3PO_4 . The resulting solution is used to treat a fresh bath of phosphate rock.	Production of concentrated phosphate fertilizer.
389,566	1888	Glaser, Chas.	Mineral phosphate, H ₂ PO ₄ .	Finely ground phosphate rock is treated with H_3PO_4 and allowed to cure.	Production of double acid phosphate.
417,820	1889	Do.	Phosphate rock, H ₂ PO ₄ .	Na_2SO_4 is dissolved in H_3PO_4 . CaCO_3 is added to solution.	Production of NaHPO_4 and gypsum.
504,453	1893	Mejer, Theo.	Na_2SO_4 , H ₂ PO ₄ , CaCO_3 .	Ingredients are mixed and boiled, temperature being held below 115° C. Mass is dried, grummi, and sifted.	Production of double acid phosphates free from pyrophosphoric acid.
631,181	1899	Schuler, G.	Phosphate rock, H ₂ PO ₄ , heat.	Phosphate rock is dissolved in cold H_2SO_4 . The free SO_2 is then eliminated by boiling and a mixture of CaHPO_4 and CaSO_4 is precipitated. After separation, H_2SO_4 or some other acid is added to the precipitate.	Production of CaHPO_4 free from sulphates.
852,372	1907	Bergmann, E.	Phosphate rock, water, SO_2 and P_2O_5 , HCl, or H_2SO_4 .	Phosphate rock is treated with HNO ₃ obtained by oxidizing atmospheric nitrogen.	Production of soluble phosphoric acid.
872,757	1907	Schlutius, J.	Phosphate rock, HNO ₃ , or other oxides of nitrogen.		

TABLE LXVI.—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES BY TREATMENT WITH ACIDS OTHER THAN SULPHURIC—Continued.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
902,425	1908	Machalske, F. J.	Phosphate rock, SO_2 , H_2O , heat.	Phosphate rock is subjected to action of SO_2 in presence of small quantity of water. Soluble material then dissolved in water saturated with SO_2 . Residue of CaSO_3 is then calcined.	Production of soluble phosphate by means of action of SO_2 on phosphate.
997,968	1911	Cusatelli, G.	Phosphate rock, H_2SO_4 , HNO_3 .	Phosphate rock is treated in the usual manner with H_2SO_4 to which a small quantity of HNO_3 is added.	Production of rich phosphate fertilizer which does not readily revert.
1,011,909	1911	Bretteville, A.	Phosphate rock, HNO_3 , lime.	Phosphate rock is dissolved in HNO_3 . Lime is added to the solution and precipitate separated by decantation or filtration.	Production of phosphate fertilizer containing $\text{Ca}(\text{NO}_3)_2$.
1,018,746	1912	Dittmar, Max	Metallic phosphate, halogen acid.	Metallic phosphate is treated with a concentrated halogen acid (HCl) until the metallic halogen compound is formed. It is then filtered.	Production of phosphoric acid.
1,037,876	1913	Peacock, Samuel	Phosphate rock, gases or vapors containing nitric acid, water.	Phosphate is ground and immersed in water. Nitric acid gases are led in.	Production of material containing calcium nitrate and dicalcium phosphate.
1,038,145	1913	Braun, F. W.	Phosphate rock which consists principally of tricalcium phosphate and calcium carbonate.	Phosphate is ground and mixed with HNO_3 .	Production of a fertilizer containing monocalcic phosphate and calcium nitrate.
1,020,153	1912	Newberry, S. B., and Barrett, H. N.	Phosphate rock, H_2SO_4 , HCl , heat.	Phosphate rock is treated with H_2SO_4 and HCl . The solution is filtered from the CaSO_4 and evaporated to dryness. HCl is evolved and used again.	Production of CaH_2PO_4 .
1,078,887	1913	Willson, T. L., and Haft, M. M.	Phosphate rock, pyrophosphoric acid.	Phosphate rock is mixed with a solution of pyrophosphoric acid. A dry, easily disintegrated cake is produced.	Method of making double superphosphate.
1,083,429	1914	Brunswick, F.	Phosphate material, acid.	Treat material with less dil. sulphuric acid (or acid stronger than phosphoric) than is required for the calcium of phosphate and stopping reaction before impurities go into sol. Separate liquid and treat with additional acid, then take up excess acid with bone black.	Production of phosphoric acid.
1,235,025	1917	Glaeser, W.	Phosphate rock, HCl , heat, $\text{Ca}(\text{OH})_2$.	Phosphate rock is treated with hydrochloric acid under heat.	Production of citrate soluble dicalcium phosphate.
1,246,636	1917	Meyers, H. H.	Phosphate material, SO_2 , SO_3 , O_2 , gases.	Mixture is cooled to 30°C . and treated with calcium hydrate to secure amorphous dicalcium phosphate. Moistened ground phosphate material is subjected to the action of SO_2 and SO_3 gases in presence of oxygen.	Production available phosphate.
1,251,741	1918	Blumenberg, Jr., H.	Tricalcium phosphate, SO_2 .	Ground tricalcium phosphate is subjected to SO_2 in presence of water to form calcium sulphite and phosphoric acid and separating products.	Production of phosphoric acid.

TABLE LXVI.—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES BY TREATMENT WITH ACIDS OTHER THAN SULPHURIC—Continued.

U.S. Pat. No.	Date	Patente	Reagents Used	Treatment	Object of Process
1,292,293	1919	Foss, A.	Phosphate containing some calcium carbonate, HNO_3 .	Phosphate material containing some calcium carbonate is treated with nitric acid and while in the semi-liquid state, a current of air is passed through the mass.	Production of a phosphate fertilizer containing nitrogen.
1,297,464	1919	Hechenbleikner, I.	Waste gases from acid phosphate plants, solution of hydrosilicic acid.	Waste gases containing silicon fluoride are passed in contact with a solution containing gelatinous hydrosilicic and hydrofluosilicic acids.	Recovery process for waste gases.
1,313,379	1919	Do.	Phosphate rock, hydrofluosilicic acid, hydrofluoric acid.	Phosphate rock is treated with a dilute mixture of hydrofluosilicic and hydrofluoric acids and phosphoric acid separated from impurities.	Production of phosphoric acid.
1,326,533	1919	Sadtler, S. S.	Phosphate rock, SO_2 gas, steam, pressure.	Ground phosphate rock is subjected to SO_2 gas with steam under pressure.	Production of dicalcium phosphate containing about 1% monocalcium phosphate substantially free from free acid. Production of acid sodium pyrophosphate.
1,383,990	1921	Kelly, A.	Sodium pyrophosphate, $NaCl$, acid (HCl).	Sodium pyrophosphate is treated with HCl to produce acid sodium pyrophosphate which is salted out with sodium chloride.	Process for rendering crude phosphates available.
1,428,259	1922	Rusberg, F.	Phosphate rock, lignite or infusorial earth, alkali sulphate, water, sand and hydrochloric acid gas.	100 parts of phosphate, 40 parts of lignite, and 50 parts of sand are mixed and treated with hydrochloric acid gas and steam. The product is then mixed with 80 parts ammonium sulphate. Product contains 12% water soluble P_2O_5 and 5% nitrogen.	Process for producing sodium pyrophosphate and hydrochloric acid.
1,447,544	1923	Glaser, W.	Phosphate rock, niter cake (Na_2HSO_4), sodium chloride, filter, heat.	Phosphate rock is treated with a solution of sodium acid sulphate and sodium chloride. Calcium sulphate is filtered off, and the filtrate evaporated and ignited at 500° C. driving off hydrochloric acid.	Process for the production of double-superphosphate.
1,475,959	1923	Meyers, H. H.	Phosphate rock, sulphuric acid, Dorr agitators and thickeners, dryer and disintegrator.	A slurry of phosphate rock and dilute phosphoric acid (phosphoric acid made by Dorr process) is fed to a direct heat rotary dryer where the chemical reaction takes place. The product is discharged dry to disintegrate.	Process for the production of acid phosphate and alkali metal nitrate.
1,517,687	1924	Voerkelius, G. A.	Phosphate rock, nitric acid, potassium sulphate and suitable mixing and grinding apparatus.	Phosphate rock is decomposed with nitric acid in the presence of potassium sulphate forming calcium acid phosphate, calcium sulphate and potassium nitrate. A dry product is obtained which is easily ground.	Process for increasing the availability of the P_2O_5 in phosphate rock.
1,530,397	1925	Oden, S. L. A., and Sakera, F.	Phosphate rock, peat, caustic soda, acid, burnt pyrites, dryer, grinder, etc.	Peat is treated with caustic soda and ground with phosphate rock and nitric acid (sufficient to give a hydrogen concentration of 5 to 1). The mass is heated to 200° C. under pressure, neutralized with lime and mixed with burnt pyrites which acts as a catalyst to hasten the reaction.	

TABLE LXVII.—PROCESSES FOR THE PRODUCTION OF PHOSPHORIC ACID BY COMBINED ACID AND HEAT TREATMENT.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
75,326	1868	Wilson, G. F.	Bones, heat.	Bones are burned.	Burning puts bones into better condition for acid treatment.
283,426	1883	Scribner, E. A.	Aluminum or iron phosphate, SO_2 , heat.	Mixture of phosphate and S is roasted, or SO_2 is passed through heated phosphate.	Production of available P_2O_5 .
382,604	1888	Goodale, S. L.	Minerals containing considerable quantities of hydrated alumina or ferric phosphate or both, carbonaceous material, H_2SO_4 , heat.	Mineral is powdered and mixed with carbonaceous material previously moistened with H_2SO_4 . Mass is then heated.	Production of available phosphate.
446,087	1891	Ruymbeke, J. Van	Aluminum and iron phosphates, H_2SO_4 , heat.	Phosphate is treated with H_2SO_4 as usual, and then heated until it assumes a gray color.	Production of a metaphosphate containing sulphate of both iron and alumina.
446,998	1891	Do.	Phosphate, K_2SO_4 or KCl , H_2SO_4 , heat.	Phosphate is powdered, and K_2SO_4 and H_2SO_4 added. The mixture is then heated.	A product which is highly soluble in water, free from acidity, and nondeliquescent.
462,366	1891	Simpson, J.	Tricalcic or dicalcic phosphate, HCl , sulphate of soda, water, heat, caustic lime.	Phosphate is dissolved in HCl and a solution of sulphate of soda added. Supernatant liquor is drawn off and concentrated, the evolved HCl being condensed. The pasty liquor is now heated and then run into water. This solution contains phosphate and chloride of soda which are "salted out" separately. The phosphate of soda is dissolved and treated with caustic lime. Lime phosphate separates out and caustic soda remains in solution.	Production of caustic soda and, if desired, lime phosphate.
852,371	1907	Bergmann, E.	Phosphate rock, water, SO_2 , $\text{CaH}_2(\text{PO}_3)_2$, heat.	Phosphate rock is dissolved in cold H_2SO_4 . The solution is then boiled and CaHPO_4 precipitated. $\text{CaH}_2(\text{PO}_3)_2$ is then added to filtrate, resulting in precipitation of more CaHPO_4 .	Production of CaHPO_4 .
995,028	1911	Newberry, S. B., and Barrett, H. N.	Phosphate rock, H_2SO_4 , heat.	Phosphate is pulverized and mixed with H_2SO_4 . Mixture is calcined in an oxidizing atmosphere. This decomposes the CaSO_4 with liberation of SO_2 and O . Material is then ground.	Production of a citrate-soluble material containing calcium pyrophosphate and free lime.
1,024,880	1912	Coates, L. R.	Native phosphates, limestone, heat, H_2SO_4 .	Phosphate and limestone are powdered and mixed. The mixture is calcined and then slaked with H_2SO_4 , only enough acid being used to leave the material as a dry powder.	Production of a fertilizer.
1,034,090	1912	Dunham, H. V.	Phosphate rock, H_2SO_4 , water.	Ingredients are mixed thoroughly and calcined.	Production of citric-soluble P_2O_5 .
1,255,829	1918	Blumenberg, Jr., H.	Phosphate material, acid hydrocarbon sludge, heat.	Phosphate material is treated with an acid hydrocarbon sludge containing enough H_2SO_4 to convert phosphate material to phosphoric acid. Heat until all of volatile matter is driven off. Treat the residue with a calcareous phosphate in presence of water.	Production of superphosphate containing gypsum, and finely divided carbon.

TABLE LXVIII—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES BY DECOMPOSITION WITH A SILICATE, ALKALI, OR ALKALINE EARTH

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
45,961	1865	Liebig and Cooper	Aluminum or iron phosphate lime soda or potash	Phosphate is heated with lime	Production of an alkaline phosphate
74,799	1868	Commins, John	Phosphate minerals heat, solution of common salt	Phosphate is heated and then saturated with the salt	Production of soluble phosphate
78,061	1868	Do	NaCl solution, gas liquor, phosphate rock	Phosphate is treated with NaCl solution heated, and the mixture is then saturated with the salt	Production of soluble or available P_2O_5
90,057	1869	Stewart, David	Phosphate rock, potash solution, lime gypsum	Phosphate is heated with caustic potash solution in a lime composition, the mixture is then dried	Production of "the persicator"
102,408	1870	Sapp, W. I.	Phosphate, gas liquor or bones etc waterglass	Phosphate is heated with lime	Production of water soluble phosphate
110,994	1871	Prescott D. W.	Bone dust (1,600 pounds soda ash (300 pounds), water (12 to 20 gallons))	Bone dust is heated with lime	Production of soluble phosphate
123,743	1872	Tanner Benjamin	HClO ₄ , NaCl heat	HClO ₄ is treated with NaCl	Production of sodium phosphate
232,029	1882	Gibbons and Liebig	Aluminum or iron phosphate soda or potash salts carbonaceous matter	Aluminum or iron phosphate is treated with soda or potash salts	Method of increasing the availability of P_2O_5
284,674 446,815	1883 1891	Rocour, Georges Glaser, Charles	Phosphoric slag, coal Na ₂ CO ₃ , lime phosphoric acid, alkali salt	Phosphoric slag is heated with Na ₂ CO ₃ and lime	Production of Na ₂ PO ₄
453,299	1891	Do	Aluminum phosphate alkali solution heat CO ₂ lime	Aluminum phosphate is heated with alkali solution and CO ₂	Process of making alkaline phosphate
453,300	1891	Do	Aluminum phosphate carbonate or phosphate of an alkali water heat	Aluminum phosphate is heated with alkali carbonate or phosphate	Production of citrate soluble aluminum phosphate
542,080	1895	David David I.	Phosphate rock containing SiO ₂ and CaCO ₃ (should they are not contain these are added) heat salt of an alkali	Phosphate rock is heated to a point below fusion but above temperature of decomposition of CaCO ₃ . Addition of a salt if an alkali lowers necessary temperature	Production of citrate soluble phosphate
588,266	1897	DeChalmot, G.	Phosphate rock electric current and water	Phosphate is heated and fused in an electric furnace	Production of citrate soluble phosphate
589,197	1897	Stead J. E.	Natural phosphates siliceous and calcareous matter	The fused mass runs out and falls upon sand. It is then dumped into water. Materials are melted together	Phosphate soluble in solvents existing in the soil

TABLE LXVIII.—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES BY DECOMPOSITION WITH A SILICATE, ALKALI, OR ALKALINE EARTH—*Continued*.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
598,182	1898	Poole, Herman	Native aluminum phosphate, heat, caustic soda solution, aqueous solution of sodium silicate, H_2SO_4 .	Phosphate is boiled in caustic soda solution. It is then filtered and the filtrate mixed with sodium silicate solution. Alumina is thus precipitated as silicate. The sodium phosphate remaining in solution is crystallized out. The aluminum silicate is heated with H_2SO_4 , yielding aluminum sulphate. Mixture is heated.	Production of tribasic sodium phosphate and aluminum sulphate.
601,089	1898	Wiborgh, J. G.	Apatite, carbonate of sodium or potassium or caustic soda or potash, heat.	Materials are melted together.	Production of citrate-soluble tetracalcium sodium (or potassium) phosphate.
721,489	1903	Wolters, Wilhelm	Phosphorites or bone, silicates of alkaline earths and alkalies, heat.		Production of citrate-soluble phosphate.
917,502	1909	Strickler, E. H.	$NaHSO_4$, phosphate rock, heat.	Phosphate rock is dissolved in a solution of $NaHSO_4$ and Na_2SO_4 , crystallized out.	Process of separating Na_2SO_4 from $NaHSO_4$.
922,494	1909	Lowman, J. W.	Phosphate rock or bones, etc., $NaCl$, dolomite, fluorspar, heat, water, potash.	Phosphate is pulverized, and dolomite and fluorite are burned and pulverized. All are mixed with $NaCl$ and water. The mass is then heated. Potash is added when the phosphate rock is highly siliceous.	Production of available phosphate.
931,846	1909	Connor, J. H.	Phosphates, Na or K hydroxides or carbonates, Ca or Mg or Ba hydroxides, water, Na_2CO_3 , Na_2HPO_4 , caustic soda, water.	Ground phosphate is mixed with alkali, alkaline earth, and water. This mixture is heated and then ground.	Production of available phosphate.
950,159	1910	Ridenour, W. E.		Mix Na_2CO_3 , Na_2HPO_4 , and caustic soda with water, insufficient to dissolve the Na_2CO_3 .	Manufacture of trisodium phosphate with hydrated sodium carbonate.
972,567	1910	Newberry, S. B.	Natural phosphates or bones, etc., phosphoric acid or water-soluble phosphates such as those of Na or K , heat.	Mixture is calcined and ground.	Production of citrate-soluble phosphate.
978,193	1910	Do.	Phosphate rock or bone, lime, soda or potash carbonate as flux, heat.	Materials are mixed, calcined, and ground.	Do.
991,096	1911	Schroder, Heinrich	Aluminum, iron, and calcium phosphates, Mg or Ca chlorides, water, heat, $NaCl$.	Phosphate and chloride are mixed and heated with exclusion of air after the principle of fractional sublimation. Above $100^\circ C$, the vapors are led into $NaCl$ solution and aluminum sodium chloride is formed. Above $183^\circ C$, HCl is formed and condensed. Above $280^\circ C$, ferric chloride is formed, which may be decomposed into ferric oxide and HCl by steam. The residue in the furnace contains the alkali earth phosphate formed. If $MgCl_2$ has been used, the phosphate formed is soluble in citrate solution. If $CaCl_2$ has been used, the phosphate must be treated (HCl treatment) to render it soluble.	Do.

TABLE LXVIII.—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES BY DECOMPOSITION WITH A SILICATE, ALKALI, OR ALKALINE EARTH.—Continued.

U. S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
005,504	1911	Palmaer, W.	HCl, NaOH, phosphate rock.	Phosphate rock is dissolved in HCl and NaOH added to precipitate.	Production of citrate-soluble P_2O_5 .
1,002,198	1911	Freerichs, F. W.	Calcium phosphate, ammonium sulphate, heat, H_2SO_4 , water.	Phosphate and ammonium sulphate are mixed and roasted. Ca pyrophosphate is obtained, ammonia being driven off. The pyrophosphate is treated with H_2O and water, $Ca(PO_3)_2$ and $CaSO_4$ being obtained.	Production of a fertilizer.
1,016,352	1912	Meriwether, C. N.	Natural phosphate, carbonate or fluoride of lime, heat, water, potash granite or magnesite.	Phosphate is mixed with the lime compound, and the mass fused. It is then run into water and ground.	Do.
1,016,989	1912	Galt, H. A.	Lime mud (a mixture of $CaCO_3$ and NaOH obtained as a by-product in the manufacture of caustic soda), phosphate rock, heat.	Brush-granite or magnesite may be added. Lime mud and phosphate are mixed and heated.	Production of soluble phosphate.
1,035,619	1912	Giese, F., and Wolters, W.	Natural phosphate, artificial silicates for their raw materials, such as acid sodium sulphate, limestone, and sand), heat, steam, air.	Phosphate and artificial silicate are melted together, and the melted mass is finely distributed by a blast of mixed steam and air.	Production of citrate-soluble phosphate.
1,037,837	1912	Strickler, E. H.	Phosphoric acid, alkali sulphate, carbonaceous matter, heat.		
1,042,400	1912	Connor, J. H.	Phosphate rock or bones, etc., limestone, soda, iron oxide (flue dust) or sodium sulphate, water, heat.	Dilute phosphoric acid is treated with an alkali sulphate and carbonaceous matter, then furnace to produce tri alkali phosphate.	Process of making tri alkali phosphate.
1,042,401	1912	Do.	Phosphate rock or bones, etc., soda ash or sulphur soda ash, iron oxide (flue dust) as a flux, heat, water.	Materials are mixed, and, in a wet state, subjected to a high temperature. It is then ground.	Production of available phosphate.
1,042,402	1912	Do.	Phosphate rock or bones, etc., sodium salts, heat, water, iron oxide (flue dust).	Materials are mixed and heated.	Do.
1,042,588	1912	Do.	Phosphate rock or bones, etc., sodium salts, heat, water, iron oxide (flue dust).	Materials are mixed, heated, and ground.	Do.
1,046,327	1912	Newberry, S. B., and Barrett, H. N.	Natural phosphates, alkali sulphates, water, heat.	Materials are mixed and heated in an oxidizing atmosphere.	Production of citrate-soluble phosphate.
1,058,249	1913	Meriwether, C. N.	Phosphate rock, lime rock, heat, compound of Na or K, etc. Iron oxide dolomite may be added.	Mix materials in proportions to form potassium pyrophosphate. Heat to about $1500^{\circ}C$, then quench with water, crush and treat with steam under pressure. Phosphate and lime rock are mixed, ground, and heated. Mass is then run out, combined with Na and K compounds, ground, again heated, and reground.	Production of potassium hydrogen phosphate. Production of a fertilizer.

TABLE LXVIII.—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES BY DECOMPOSITION WITH A SILICATE, ALKALI, OR ALKALINE EARTH—Continued.

U. S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
1,074,779	1913	Dunham, H. V.	Phosphate rock, alkali carbonate, alkali sulphate, heat.	Mix materials and heat to white heat.	Production of citrate soluble P_2O_5 .
1,074,808	1913	Newberry, S. B., and Barrett, H. N.	Insoluble phosphate gypsum, carbonate matter, heat.	Grind together insoluble phosphate, gypsum and carbonate matter (each equal to two thirds of P_2O_5 present), then calcine until gypsum is decomposed and carbonate matter oxidized.	Process of making a fertilizer.
1,076,200	1913	Dunham, H. V.	Phosphate rock, salt of an alkali metal alumina, heat.	Phosphate rock, salt of an alkali metal and a "non flux" (Al_2O_3) are calcined at white heat for one hour.	Production of citrate available P_2O_5 .
1,076,497	1913	Haff, M. M.	Natural phosphate (100), non-feldspathic aluminum silicate (60), electric furnace.	A mixture of natural phosphate and non feldspathic aluminum silicate is fused in an electric arc furnace.	Process of separating phosphoric acid from natural phosphates.
1,094,857	1914	Landis, W. S.	Phosphate material, sodium salt, water, heat.	Mix phosphate material, sodium salt and water, heat rapidly and calcine.	Production of available phosphates.
1,099,151	1914	Nicholas, T. C.	Potassium bearing silicate, phosphorus bearing mineral and calcium sulphate.	Finely divided and mixed.	Production of a fertilizer.
1,103,059	1914	Landis, W. S.	Phosphate rock, Na_2SO_4 or Na_2CO_3 , water, C.	Mixture is burned while air is being blown through.	Production of soluble or available P_2O_5 .
1,111,490	1914	Perino, Josef	Potash containing silicate phosphate rock, $MgCl_2$, heat, steam, water.	Product is pulverized. Mixture is heated in presence of steam. Product is treated with sufficient water to cool and hydrate the same and leave a dry powder.	Production of a fertilizer.
1,120,917	1914	Downs, W. F.	Finely divided silica, heat.	Mixture is heated.	Production of citric-soluble phosphate.
1,121,160	1914	Beckman, J. W.	Non-volatile alkali salt (aluminate, etc.), mineral phosphate, heat.	Heat mixture to redness, and dissolve out soluble phosphate.	Production of soluble phosphate.
1,126,408	1915	Cowles, A. H.	Phosphate rock, feldspar, heat, acid.	Heat potash or other feldspar with phosphate rock to softening temperature. Treat residue with acid or solvent which will not produce insoluble phosphate or aluminate.	Production of available phosphates.
1,137,065	1915	Landis, W. S.	Tri calcium phosphate, sodium salt, carbon, heat.	Mix tricalcium phosphate, sodium salt and carbon, and heat to drive off acid radical of sodium salt, and then heat to incipient fusion.	Production of citrate soluble phosphoric acid.
1,144,405	1915	Willson, T. L., and Haff, M. M.	Alkali mineral, SO_3 , alkaline earth phosphate, heat.	Materials are fused and the fused mass treated with suitable reagent to dissolve the alkali phosphate, or fused mass finely ground.	Production of a fertilizer containing an alkali.
1,149,390	1915	Meriwether, C. N.	Phosphate material, iron, lime and magnesia salts, K_2O , Na_2O , heat.	Mix phosphate material, iron, lime and magnesia salts, and fuse in furnace. To molten mass add potash and soda oxide. Grind and use with or without extracting the iron.	Production of a basic phosphate fertilizer.

TABLE LXVIII.—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES BY DECOMPOSITION WITH A SILICATE, ALKALI, OR ALKALINE EARTH—*Continued*.

Date	Patentee	Reagents Used	Treatment	Object of Process
1915 1,553,711	Newberry, S. B., and Barrett, H. N.	Phosphate rock, alkali metal salt, heat.	Phosphate rock and an alkali metal salt are calcined to a temperature where alkali metal salt is volatilized.	Production of citrate soluble phosphate.
1,162,802	Do.	Natural phosphate, alkali metal salt, heat.	Calcine materials until all acid radical of alkali metal salt, and part of alkali metal oxide formed, is volatilized.	Process of rendering natural phosphates citrate soluble.
1,162,944	Do.	Natural phosphate of lime, alkali metal compound, heat, rotary kiln.	Materials are calcined until volatile constituents and part of alkali metal oxide are volatilized. The materials are constantly agitated (by rotary kiln) while hot gases pass through.	Production of citrate soluble phosphate.
1,161,130	Connor, J. H.	Blatt furnace slag, phosphoric material, soda ash, lime, feldspar, heat.	Materials are ground, mixed, and calcined to render phosphate and potash partly water soluble.	Production of a fertilizer.
1,172,420	Bassett, H. P.	Phosphate rock, feldspathic rock, alkali metal acid sulphate, carbonaceous material, heat, special type of rotary furnace.	The feldspathic rock is heated with alkali metal acid sulphate rendering potash water soluble. Phosphate rock is treated with the acid fumes evolved and P_2O_5 made available. A special type of furnace is used.	Production of soluble potash and phosphate.
1,173,303	Newberry, S. R. and Barrett, H. N.	Natural phosphate, alkali metal bisulphate, heat.	Materials are mixed and heated until SO_2 is evolved and the residual phosphate rendered citrate soluble.	Production of citrate soluble phosphate.
1,174,176	Do.	Natural phosphate, alkali metal chloride, a material yielding SO_2 at temp. of calcination, heat.	Natural phosphate and an alkali metal chloride are heated together in a rotating kiln through which combustion gases containing SO_2 pass counter current to direction of charge. The chloride is decomposed and chlorine passes off and is collected. The residue is ground and used as fertilizer.	Production of citrate soluble phosphate.
1,194,219	Newberry, S. R., and Fishburne, G. R.	Insoluble phosphate, alkali metal compound, heat, rotary kiln.	Finely ground insoluble phosphate, and an alkali metal compound are heated to low red in a rotary kiln.	Production of a citrate soluble phosphate.
1,204,238	Bishop, E. S.	Phosphate rock, metal chloride, silica, steam, rotary kiln, heat.	Heat finely ground phosphate rock, metallic chlorides, and silica which have been moistened with steam in a rotary kiln until silica combines with the metal of chloride and part of calcium in phosphate.	Production of available phosphates.
1,214,008	Ciselet, E., and De- guede, C.	Natural phosphate, calcium chloride, heat.	Treat finely ground phosphate with a concentrated solution of $CaCl_2$. Dry and melt at about $1000^\circ C$. Grind and wash out $CaCl_2$ and recover from wash.	Production of a phosphate available to plants.
1,214,346	Messerschmitt, A.	Potash bearing mineral, phosphate, limestone, nitrate, heat, kiln.	Phosphate material, a potash bearing mineral and limestone are calcined and then treated with 25% $Ca(NO_3)_2$ in hot solution, and dried.	Production of non-hygroscopic fertilizer.

TABLE LXVIII.—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES BY DECOMPOSITION WITH A SILICATE, ALKALI, OR ALKALINE EARTH—*Continued*.

U. S. Pat. No.	Date	Patente	Reagents Used	Treatment	Object of Process
1,229,684	1917	Volpato, V.	Phosphate rock, dolomite, sodium carb-nate, sodium sulphate, heat.	100 parts of phosphate (60% B.P.L.) and 6 parts of mixture of, dolomite, 25% Na ₂ CO ₃ , 35% Na ₂ SO ₄ , are heated to a temperature of about 750° C. The calcined mass is treated with water.	Production of available phosphate.
1,236,812	1917	Zilk, J. E.	Phosphate rock, coke, limestone, flux, heat, rotary kiln.	Finely ground phosphate rock, coke, limestone and flux are heated in rotary kiln by coke contained in mixture to about 1300 to 1400° F. Materials are mixed, heated to incipient fusion by combustion of coke in mixture.	Production of available phosphate.
1,247,059	1917	Do.	Phosphate rock (20), coke (2-3), limestone (2-3), niter cake (4), heat.		Production of a phosphate fertilizer.
1,267,473	1918	Storpani, E., and Volpato, V.	Phosphorite, alkali oxygen salt (Na ₂ CO ₃), heat.	A mixture of phosphorite (60 parts Ca ₃ (PO ₄) ₂) and sodium carbonate (to parts) is roasted at 600° C. The mixture is then hydrated while still hot.	Process of making a phosphate fertilizer.
1,276,555	1918	Meadows, T. C.	Hydrous potassium mineral (Glaucinite) acid phosphate.	A hydrous potassium mineral (such as glaucinite) is ground and mixed with water to form a sludge, which is treated with commercial acid phosphate to form a potassium phosphate.	Production of mono and di potassium phosphate.
1,281,681	1918	Soper, E. C.	Phosphate material, alkali metal salt, special calcining apparatus, heat.	Phosphate material, and an alkali metal salt are mixed with water to form a thin paste. This paste is flowed onto a highly heated surface to form a uniform layer. The moisture is quickly driven off, leaving a porous mass which is subjected to a calcining temperature. Materials are heated to about 1100° C.	Production of a citrate soluble phosphate.
1,282,385	1918	Delacourt, A. F.	Tri calcium phosphate material, potassium containing silicate, silica, heat.		Production of available phosphoric acid and potash.
1,282,805	1918	Gardiner, R. F.	CaCl ₂ , P ₂ O ₅ , potassium bearing mineral, wood waste, heat.	The mixed materials are heated to a bright red.	Production of a fertilizer containing available P ₂ O ₅ and potash.
1,293,220	1919	Shuey, P. MacG.	Phosphate material, niter cake.	Phosphate material is mixed with molten niter cake and allowed to act.	Production of a phosphate fertilizer.
1,310,080	1919	Henwood, A.	Phosphate rock, acid sulfate, potash aluminum silicate, niter cake.	Finely ground phosphate rock or potash silicate, mixed with acid sulfate or niter cake is subjected to a fine spray of water sufficient to hydrate the calcium sulfate formed.	Production of phosphate and potash fertilizers.
1,366,569	1921	Kreiss, A. L.	Phosphate material, potassium bearing silicate, alkali metal salt, heat.	Phosphate material, potassium bearing silicate and more than one alkali metal salt are mixed and calcined. Soluble phosphate and potash are leached out.	Process and production of a soluble phosphate and potash fertilizer.
1,372,051	1921	Tromp, F. J.	Iron or aluminum phosphates, caustifiable alkali metal and lime compound, water.	Phosphates are treated with a caustifiable alkali, metal and lime compound in the presence of water, in proportions 4 parts carbonate, 20 parts P ₂ O ₅ , 30 parts CaO.	Production of citrate soluble phosphate fertilizer.

TABLE LXVIII.—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES BY DECOMPOSITION WITH A SILICATE, ALKALI, OR ALKALINE EARTH—*Continued.*

U. S. Pat. No.	Date	Patente	Reagents Used	Treatment	Object of Process
1,379,735	1921	Walker, G. T.	Sodium bisulphate, phosphate rock, soda ash, caustic soda.	Mix a solution sodium bisulphate with phosphate rock to form acid phosphate and Glauber's salt, and adding soda to this solution until neutral, to produce neutral sodium phosphate. Filter and cool solution and separate crystals of Glauber's salt. Caustic soda is then added to solution to produce tri sodium phosphate.	Process of making Glauber's salt, tri sodium and neutral sodium phosphate.
1,387,151.	1921	Glaeser, W.	Phosphate rock, Na_2CO_3 , carbon, carbonic acid, sand.	Phosphate rock, Na_2CO_3 , carbon and sand are heated with a low red heat, and soluble phosphate leached out with water and carbon dioxide passed through it. The Na_2CO_3 is crystallized out.	Method of treating phosphate rock to render phosphate water soluble.
1,396,149	1921	Soper, E. C.	Phosphatic material, combustible binder (pitch), alkali metal salt, calcium carbonate, rotary kiln, heat.	Phosphatic material is mixed with a combustible binder, with or without an alkali salt or calcium carbonate briquetted and heated in rotary kiln.	Process of treating phosphate rock to render phosphate citrate soluble.
1,396,975	1921	Do.	Phosphatic material, sawdust, alkaline earth compound, Na_2SO_4 , heat, rotary kiln.	Phosphatic material rendered fluid by mixture of water and Na_2SO_4 is suffused with carbonaceous matter (sawdust) and alkaline earth compound and is heated to about 2300 to 2600° F. in a rotary kiln.	Process of treating phosphate rock to render phosphate citrate soluble.
1,411,696	1922	Haegre, T.	Natural phosphates, potassium bearing silicates, marl, heat.	Materials are broken up, mixed, and melted, and disintegrate by high pressure fluid, collecting melt and grinding the fine particles.	Production of a potash and phosphate fertilizer.
1,413,168	1922	Kreiss, A. L.	Phosphate rock, alkali salt, rotary drier.	Phosphate rock heated highly and plunged into solution of potassium or sodium salt explodes allowing an intimate mixture to be formed, which is further calcined in reducing atmosphere in rotary drier.	Production of a fertilizer containing potash or sodium and available phosphate.
1,437,456	1922	Soper, E. C.	Phosphate rock (100 parts), nitric acid (22.5 parts), calcium carbonate (7.5 parts), saw dust (7.5 parts), rotary kiln, heat.	A mixture of phosphate rock, carbonaceous matter and an alkali metal salt are calcined in a rotary kiln at 2400 to 2600° F.	Production of citrate soluble P_2O_5 .

TABLE LXIX.—PROCESSES TO BE USED IN CONNECTION WITH THE IRON AND STEEL INDUSTRIES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES.

U.S. Pat. No.	Date	Patente	Reagents Used	Treatment	Object of Process
284,674	1883	Rocour, G.	Phosphatic slag, flux, lime, Na_2SO_4 , H_2SO_4 , coal or coke, pyrites, H_2O .	The slag is first fused under reducing conditions. (1) The matte is blown in a basic converter with the addition of lime and small quantities of Na_2SO_4 . (2) Matte is mixed with Na_2SO_4 and coal and heated in reverberatory furnace in reducing flame, oxidizing flame being used later. Mass is then lixiviated. The alkaline chlorides are blown into the phosphorus iron in a Bessemer converter along with steam, water gas, or other hydrogen-yielding substance. Resulting slag is lixiviated and lime added to the solution. Molten metal is poured upon an alkali carbonate in a basic Bessemer furnace. More Na_2CO_3 is introduced by the blast. The slag is then run off and lixiviated.	Methods of obtaining soluble alkaline phosphates.
301,406	1884	Thomas, S. G.	NaCl or KCl , iron containing over 1 per cent P, superheated steam or water gas, Fe_2O_3 , H_2O , lime, air, heat.	The alkaline chlorides are blown into the phosphorus iron in a Bessemer converter along with steam, water gas, or other hydrogen-yielding substance. Resulting slag is lixiviated and lime added to the solution.	Production of precipitated phosphate of lime from phosphorus-bearing iron.
301,407	1884	Do.	Molten pig iron containing P, Na_2CO_3 , NaNO_3 , lime, H_2O , heat.	Molten metal is poured upon an alkali carbonate in a basic Bessemer furnace. More Na_2CO_3 is introduced by the blast. The slag is then run off and lixiviated.	Production of alkaline phosphate from phosphorus-bearing iron.
306,664	1884	Thomas, S. G., and Twinman, T.	Slag containing iron oxide and P_2O_5 , HCl , oxidizing agent, lime, H_2SO_4 , H_2O , heat.	Slag is first treated with HCl , ferrous oxide in solution is then oxidized by Cl or some other agent. Powdered chalk is then added to the solution, precipitating the iron as ferric phosphate. This is filtered and treated with H_2SO_4 . The H_3PO_4 is then either separated or the mixture used in the manufacture of acid phosphate.	Production of H_3PO_4 from phosphatic slag.
312,904	1885	Scheibler, Carl	Slag (phosphatic), slow cooling.	Phosphatic slag is allowed to cool very slowly.	Segregation of P_2O_5 near surface of mass.
324,471	1885	Imperator, Luige	Phosphatic slag, Na_2SO_4 , C .	Slag is melted with Na_2SO_4 and C . Resulting mass is then treated with CO_2 and lixiviated.	Production of Na_2HPO_4 and Na_2CO_3 .
353,825	1886	Scheibler, Carl	CO_2 , Slag (phosphatic), heat, H_2O , lime.	The slag is roasted in oxidizing flame, ground, and treated with HCl . Milk of lime is added, fractionally precipitating (1) phosphates of iron, (2) the alkaline earth phosphates. The phosphates of iron are then again roasted with lime, giving phosphates of lime.	Production of phosphates of lime from slags containing iron phosphates.
361,656	1887	Twynam, Thos.	Phosphatic iron, Na_3PO_4 , Na_2CO_3 .	Na_3PO_4 is added to molten phosphatic pig iron, and Na_2CO_3 is subsequently added.	Production of soluble P_2O_5 .
372,087	1887	Reese, Jacob	Basic phosphatic slag, magnet.	Slag is pulverized and the iron separated by magnet.	Production of available P_2O_5 .
412,792	1889	Do.	The usual furnace charge, with the addition of phosphate rock.	The phosphate rock is oxidized at high temperature in the presence of lime. The slag is then withdrawn and slowly cooled.	Production of $\text{Ca}_3\text{P}_2\text{O}_8$ or available P_2O_5 .
412,793	1889	Do.	Phosphatic iron, CaO , heat.	A mixture of phosphatic iron and CaO is charged in basic Bessemer converter and slag withdrawn before iron is completely dephosphatized. Fresh lime is then added to charge.	Production of highly phosphatic slag, and subsequent dephosphatization of steel.

TABLE LXIX.—PROCESSES TO BE USED IN CONNECTION WITH THE IRON AND STEEL INDUSTRIES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES.—*Continued.*

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
535,204	1895	Howe, H. M., and Stead, J. E.....	Slag, phosphate rock, a metallic base lime, heat.	Phosphate rock is added to the molten slag in the furnace; lime is added if necessary. Slag is then run out before iron is completely dephosphorized. Slag is committed.	Production of tetracalcium phosphate.
550,024	1895	Meyer, Emil	Phosphatic slag, Na_2CO_3 .	Na_2CO_3 is added to molten slag as it issues from furnace.	Production of disintegrated slag.
714,331	1902	Reese, Jacob	Phosphatic slag, phosphate rock, CO_2 , heat.	Phosphate rock and slag are mixed and fused in a furnace in presence of oxidizing flame, gases should be largely (O_2) .	Production of fertilizer containing available P_2O_5 .
977,819	1910	Mehner, H.	Iron ore, phosphate rock, oxides of iron, lime, carbon, heat.	Iron ore and phosphate rock are heated in blast furnace, the slag produced is separated from iron rich in phosphorus. The iron is treated a second time with basic materials, giving another highly phosphatic slag.	Production of two highly phosphatic slags and elimination of phosphorus from iron.
1,002,297	1911	Merivethier, C. N....	Iron ore, phosphate rock, lime, heat, salts of Ba, K, Na, NH_4 , and Mg may be used or ferrocyanide of potash.	Phosphate rock and iron ore are intimately mixed. Mixture is then heated to redness for 1 hour to 6 hours while being agitated. Fertilizer salts may be mixed with cooled product.	Production of available P_2O_5 which may be mixed with fertilizer salts.
1,067,224	1913	Slater, O. K.	Basic slag, phosphate rock, steam, SO_2 , NH_3 .	A mixture of slag and phosphate rock is placed in a digester and steam led into mixture. The slag digesterates. SO_2 is then introduced and then NH_3 gas, materials are ground, mixed, and calcined to render phosphate and potash partly water soluble.	Production of a mixture of soluble and available P_2O_5 and $(\text{NH}_4)_2\text{SO}_4$.
1,163,130	1915	Connor, J. H.	Blast furnace slag, phosphatic material, soda ash, lime, field spar, heat.		Production of a fertilizer.
1,274,479	1918	Wenman, H. O. H..	Molten slag from steel furnace, silicate, carbon, electric furnace.	Molten slag from steel furnace is charged directly with a silicate and carbon into an electric furnace maintaining a temperature sufficient to vaporize the phosphorus.	Production of phosphorus.

TABLE LXX.—PROCESSES FOR THE PRODUCTION OF PHOSPHORUS AND PHOSPHORIC ACID BY VOLATILIZATION.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
939,428	1888	Giles, W. B., and Shearer, Arthur ..	Phosphatic material, steam, heat.	Phosphatic material is so treated as to obtain an impure phosphoric acid. This is concentrated and placed in a retort. Here it is kept at a red heat and a current of steam is passed over it. The distillate is condensed.	Process for separating phosphoric acid from impurities.
417,943	1889	Readman, J. B.....	Phosphorus-yielding material in solution, carbon, a flux, electric furnace.	The phosphorus solution is concentrated and carbon introduced. A flux may be added. It is placed in an electric furnace and phosphorus distills over.	Process of obtaining phosphorus.
452,821	1891	Wing, H. H.....	Phosphate rock, siliceous material, coal or coke, heat. Cupola furnace.	Phosphate rock is ground, mixed with the siliceous material, and molded into small balls. These are placed in a furnace with coal or coke. On heating volatilization takes place and the fumes are condensed.	Do.
540,124	1895	Ruymbeke, Jos. Van.	Natural phosphate, acid flux, reducing agent, air, heat.	Phosphate is mixed with an acid flux and a reducing agent, and heated in a blast furnace. Air is introduced into the upper part of the furnace to oxidize the phosphorus. The resultant P_2O_5 is carried to a scrubber.	Process for producing phosphoric acid.
602,747	1898	Harding, C. K.....	Phosphate base (lime), H_2SO_4 , carbon, electric furnace.	A phosphate base is treated with H_2SO_4 and bases eliminated. The phosphoric acid is then roasted to eliminate sulfur, and smelted with carbon under reducing conditions (in presence of hydrogen, etc.).	Process of making phosphorus.
689,286	1901	De Chalmot, G.....	Natural phosphate, silica, heat, moist lime, water.	Phosphate and silica are mixed and heated in an electric furnace. As fast as it becomes molten the mass is removed and brought into contact with a further quantity of silica. It is then dumped into water. Any phosphoric acid volatilized is brought into contact with moist lime.	Production of soluble phosphoric acid.
733,316	1903	Duncan, R. K.....	Phosphatic material, carbon, tar, hydrogen, heat, electricity.	Powdered phosphate is mixed with carbon and tar; the latter serving as a binder. The mixture is placed in an electric furnace. The resultant calcium phosphide is removed and placed in a chamber with hydrogen gas. Water is led in. The resultant phosphorus hydrides are dried and heated.	Production of phosphorus.
751,753	1904	Powter, N. B.....	Phosphate rock, retort, suction, heat.	Phosphate rock or aluminum phosphates are heated in a suitable retort from 200 to 1,200° F. The evolved fumes are drawn off by suction and absorbed in water.	Method of making phosphoric acid.
789,438	1905	Machalske, F. J.....	Phosphate rock, alkali-metal chloride (NaCl), carbon, heat, water.	Rock is crushed and mixed with NaCl and carbon. The mixture is heated. Phosphorus chloride is led off and treated with water.	Production of phosphorus chloride or acid and HCl, and carbides of calcium and sodium.

TABLE LXX.—PROCESSES FOR THE PRODUCTION OF PHOSPHORUS AND PHOSPHORIC ACID BY VOLATILIZATION—Continued.

U.S. Pat. No.	Date	Patente	Reagents Used	Treatment	Object of Process
789,439	1905	Machalske, F. J.	Phosphate rock, alkali-metal chloride (NaCl), carbon, nitrogen, water, heat.	Rock is crushed and mixed with NaCl and carbon. The mixture is smelted. Phosphoric chloride is given off and may be treated with water. Nitrogen is brought into contact with the charge in the furnace.	Production of phosphoric chloride or acid, HCl, and cyanamids.
789,440	1905	Do.....	Do.	As above, with the addition that the calcium sodium cyanamides are smelted with carbon and sodium carbonate.	As above, with the production of sodium cyanide in addition.
859,086	1907	Landis, G. C.	Phosphates, sand or silicate, coke, binding material, heat.	Phosphate, sand, and coke are crushed independently of each other and calcined. They are then ground, mixed, and formed into briquets with the binding material. The briquets are then fed into an electric furnace.	Process which makes excessive temperature unnecessary, prevents dust being carried over, and gives a more even action of the heat.
862,092	1907	Morehead, J. T.	Phosphate rock (calcined bones, etc.), carbon, heat.	Phosphate and carbon are heated in a furnace, and the phosphorus distilling over is condensed.	Production of phosphorus and calcium carbide, and CO.
862,093	1907	Do.....	Do.	Do.	A material containing calcium carbide and phosphide.
902,157	1908	Maywald, F. J.	Phosphate rock, electric current, air.	Electric current is passed through phosphate rock in a furnace to which air is admitted. P_2O_5 fumes condense in a hood.	Production of P_2O_5 .
939,078	1909	Peacock, S.	Phosphate rock, silica, CaO, rotary kiln.	Phosphate rock is mixed with silica or CaO to obtain a ratio of silica to alumina and ferric oxide greater than 2 and less than 4. The mixture is treated in a kiln to produce portland cement and P_2O_5 vapors.	Process of making cement and phosphorus compounds.
984,769	1911	Levi, Giorgio	Natural calcium phosphates, heat, SiO_2 , etc., anhydrous sodium salt, mineral colors.	Phosphate mixed with SiO_2 is heated in an electric furnace. Phosphoric anhydride escapes and is collected. Sodium salt added to the calcium silicate remaining in the furnace gives soluble sodium silicate. Mineral colors added to the silicate produce valuable colored material.	Production of phosphoric anhydride and calcium silicate, sodium silicate, and these latter colored.
988,137	1911	Peacock, S.	Iron oxide, phosphate rock, heat, rotary furnace.	Heat iron oxide and phosphate rock to just below fusion. P_2O_5 is liberated and calcium ferrite formed.	Process of making calcium ferrite and P_2O_5 .
997,086	1911	Do.....	Lime phosphate, silica.	Lime phosphate is mixed with silica to give chemically equivalent quantities of silica and lime. Heat till P_2O_5 is evolved.	Process of making P_2O_5 and calcium silicate.
1,000,290	1911	Do.....	Alumina (Beauxite), phosphate rock, heat, rotary furnace.	Alumina and phosphate rock are heated in a rotary furnace until P_2O_5 is driven off.	Process of making calcium aluminate and P_2O_5 .
1,000,311	1911	Washburn, F. S.	Aluminum phosphate (1000), calcium phosphate (4680), rotary kiln, heat.	Heat above 1700°C . in a rotary kiln. P_2O_5 is driven off and recovered in scrubbing towers. Residue is a cementitious product used for wall plaster.	Production of phosphoric acid.
1,015,707	1912	Peacock, S.	Calcium phosphate, calcium phosphide, heat.	Calcium phosphate is heated with calcium phosphide until P_2O_5 is driven off, which may be collected by any suitable means.	Process of making phosphorus trioxide.

TABLE LXX.—PROCESSES FOR THE PRODUCTION OF PHOSPHORUS AND PHOSPHORIC ACID BY VOLATILIZATION—Continued.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
1,018,186	1912	Haff, M. M.	Feldspar, calcium phosphate, heat.	Feldspar and phosphate are heated together in a furnace. Phosphoric acid and potash are volatilized together.	Production of potassium phosphate and a slag which may be used for glass making.
1,047,864	1912	Washburn, F. S.	Natural phosphates, SiO_2 , carbon, air, heat, water.	Phosphate, SiO_2 , and carbon are heated together in an electric furnace. Air is introduced to oxidize the phosphorus driven off. P_2O_5 is treated with water.	Production of phosphoric acid.
1,076,497	1913	Haff, M. M.	Natural phosphate, nonfeldspathic aluminum silicate, heat.	Natural phosphate and nonfeldspathic aluminum silicate are heated together in an electric arc furnace.	Production of phosphoric acid.
1,076,499	1913	Haff, M. M., and Willson, T. L.	Natural phosphate, silica, heat.	Materials fused together in an electric furnace.	Production of phosphoric acid.
1,084,856	1914	Haff, M. M.	Phosphate rock, silica, coke.	Materials are heated in an electric furnace.	Production of phosphorus and P_2O_5 .
1,100,639	1914	Washburn, F. S.	Phosphate rock, silica, carbon, heat.	Materials are heated first by fuel, then by electric current.	Production of P_2O_5 .
1,103,910	1914	Willson and Haff.	Phosphate rock, feldspar.	Materials are fused in an electric furnace.	Production of phosphoric acid and potash.
1,112,211	1914	Hechenbleikner, I.	Natural phosphate rock, siliceous material, carbon, oxygen, heat.	Materials are heated in an electric furnace, and phosphorus evolved is oxidized by oxygen and absorbed in towers by water and aqueous acid on counter current principle.	Production of phosphoric acid.
1,129,514	1915	Peacock, S.	Phosphate rock, carbon, nitrogen, heat.	Heat mixture of phosphate rock and carbon in atmosphere of nitrogen, to volatilize phosphorus and carbonitriles.	Process for producing phosphorus and fixing nitrogen.
1,129,722	1915	Do.	Natural phosphates, nitrogen, carbon, heat.	Heat mixture of phosphate and carbon in atmosphere free of oxygen, or in an atmosphere of nitrogen, collecting evolved gases and burning to produce oxides, or treating with steam under pressure to produce NH_3 and ammonium phosphates.	Production of available P_2O_5 and nitrogen.
1,142,371	1915	Schmitz, F. C.	Phosphate material, silica, carbon, heat, special absorption towers.	Phosphate material, flux, and reducing agent are fused and volatilized gases are oxidized and absorbed in special towers. The gases pass through body of liquid to remove solid matter.	Production of phosphoric acid.
1,142,397	1915	Burroughs, J. W.	Phosphate material, flux, heat, special absorption apparatus.	Fuse materials and decompose the phosphoric gas evolved by water, without cooling the gas below a predetermined temperature, in a special absorption apparatus.	Production of phosphoric acid.
1,149,233	1915	Washburn, F. S.	Phosphate rock, silica, carbon, heat, H_2SO_4 .	Phosphate rock, silica and carbon are heated in an electric furnace. The silico-phosphates of the volatilized gases are broken up by sulphuric acid and subsequently removed, leaving a pure phosphoric acid.	Production of high-grade phosphoric acid.
1,167,755	1916	Hechenbleikner, I.	Phosphate material, siliceous flux, carbonaceous material, heat.	Materials are fed to an electric furnace through a revolving passage through which the evolved gases pass preheating the charge. The carbonaceous material is fed either through the revolving passage, or to the furnace direct.	Production of phosphoric acid.

TABLE LXX.—PROCESSES FOR THE PRODUCTION OF PHOSPHORUS AND PHOSPHORIC ACID BY VOLATILIZATION—Continued.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
1,168,495	1916	Gray, Jr., J. J.	Natural phosphate, silica, carbon, metals, blast furnace.	Materials are charged into a blast furnace.	Production of phosphorus and metallic phosphide.
1,173,560	1916	Hechenbleikner, I.	Electric furnace, phosphate rock, silica, carbon.	Materials are fluxed and P_2O_5 driven out of slag.	An electric furnace for producing phosphoric acid.
1,202,937	1916	Do.	Electric furnace for production of phosphoric acid.	Special type of water cooled electric furnace for smelting phosphate rock, silica, and carbon.	Electric furnace for producing phosphoric acid.
1,217,306	1917	Do.	Electric furnace for phosphate treatment.	Special water cooled furnace. Cooled walls lined with chilled slag.	Water-cooled electric furnace.
1,226,264	1917	Schmitz, F. C.	Electric furnace.	Special water cooled electric furnace for treating phosphate rock.	Water-cooled electric furnace.
1,241,071	1917	Wagmann, W. H., Bryan, H., and Wagner, C. R.	Blast furnace for producing phosphoric acid.	A blast furnace provided with an inner charge chamber surrounded by an outer chamber in which the evolved gases burn.	Phosphate smelting blast furnace.
1,242,987	1917	Schmitz, F. C.	Phosphate rock, silica, carbon, heat, oxygen, special oxidation chamber for gases.	Phosphate rock, silica and carbon are heated and the evolved gases are passed through a tortuous path in which oxygen is introduced in direction opposite to flow of gases. The P_2O_5 gas is then absorbed in towers.	Process of oxidizing phosphorus gases.
1,274,479	1918	Wenman, H. O. H.	Molten slag from steel furnace, silicate, carbon, electric furnace.	Molten slag from steel furnace is charged directly with a silicate, and carbon into an electric furnace maintaining a temperature sufficient to vaporize the phosphorus.	Production of phosphorus.
1,282,064	1918	Wagmann, W. H., Wagner, C. R., and Bryan, H.	Mineral phosphate, silica, carbonaceous matter, fuel furnace, heat	Mix phosphate mineral with silica and carbonaceous matter. Feed this mixture down a shaft into reaction zone where volatile constituents are driven off, surrounding the central shaft, thus preheating fresh charge. Phosphorus compounds are recovered from volatile products.	Process for manufacturing phosphorus and phosphoric compounds.
1,285,575	1918	Allen, W. H.	Phosphate rock, silica, fuel, oxygen.	The finely divided mixture of phosphate, silica, fuel and oxygen is projected into combustion chamber against a shaft of refractory material.	Production of phosphoric acid.
1,290,336	1919	Hechenbleikner, I.	Combination electric furnace and mixing chamber.	Materials are charged to the mixing chamber through a rotary kiln. Coke is charged in mixing chamber directly. Materials are then pushed into electric furnace by mechanical stokers operating in mixing chamber.	Furnace for treating phosphate and other ores.
1,290,337	1919	Do.	Phosphate rock, feldspar, carbonaceous matter, electric furnace, rotary kiln.	Phosphate rock and feldspar are charged through a rotary kiln preheated by volatilized gases. Coke is charged direct. Materials are then heated to volatilize potash and phosphate. The gases are oxidized and condensed. Impurities SiO_2 and SiF_4 in gases are removed by chemical action of incoming charge.	Production of phosphate and potash fertilizer.

TABLE LXX.—PROCESSES FOR THE PRODUCTION OF PHOSPHORUS AND PHOSPHORIC ACID BY VOLATILIZATION—Continued.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
1,314,229	1919	Washburn, F. S.....	Phosphate rock, siliceous material, carbon, special shaft electric furnace.	Phosphate rock, silica, and carbon are charged into electric shaft furnace where temperature is sufficient to evolve CO and carbon dioxide. The evolved gases pass up through shaft containing fresh charge (minus carbon). Air is introduced into shaft between the CO and H_2 gases, thereby melting fresh charge before it reaches the hearth.	Production of phosphorus and $HaPO_4$.
1,334,474	1920	Waggaman, W. H.....	Natural phosphate, silica, solid fuel hinder, heat.	Materials are ground, pressed into briquettes and charged into a fuel fed furnace, where they are fused and phosphorus evolved.	Process and production of phosphoric acid.
1,359,211	1920	Washburn, F. S.....	Phosphate rock, siliceous material, coke, hearth, and electric furnace, rotary kiln, heat.	Phosphate rock and siliceous materials are fed to a hearth furnace through a rotary kiln. The material is there fused by fuel fire and run into an electric furnace where coke is admitted. The gases evolved are passed back through hearth furnace and kiln to help fuel and preheat the fresh charge. The gases are then absorbed.	Process and production of phosphoric acid.
1,360,248	1920	Brobst, G. R.....	Phosphate rock, feldspar, lime stone, iron ore, furnace slag, Na_2CO_3 , heat, NH_3 water.	Materials are calcined in a furnace and the volatilized gases are collected in cooling tank by a spray of ammonia water.	Process of rendering phosphate and potash available.
1,368,379	1921	Allen, W. H.....	Phosphate rock, sand, coke, heat.	Materials are crushed, mixed and fed up through a conduit to a highly heated reaction zone, where phosphorus is liberated, oxidized, and drawn off with other products of combustion.	Production of phosphoric acid.
1,373,471	1921	Washburn, F. S.....	Natural phosphate, siliceous material, carbon, electric furnace.	Natural phosphates, siliceous materials and carbon are fed into electric furnace where phosphorus is evolved. The burning phosphorus preheats fresh charge and is then collected.	Process of sintering phosphate charge for electric furnace treatment.
1,422,699	1922	Guernsey, E. W., and Yee, J. Y.....	Phosphate rock, sand, coal, rotary kiln, heat.	Phosphate rock, sand and coal, ground and briquetted, are heated to $1300^{\circ}C$. in a rotary kiln.	Production of phosphoric acid.
1,468,741	1923	Peacock, S.	Phosphate rock, sodium chloride, heat.	Phosphate rock and sodium chloride are heated to $1100^{\circ}C$. in a closed furnace. Phosphoryl chloride is volatilized and treated with water.	Production of phosphoric acid, hydrochloric acid, and sodium oxide.
1,492,712	1924	Klugh, B. G.....	Phosphate rock, iron potash silicate, coke, electric furnace.	Materials are proportioned to give a $CaO:SiO_2$ ratio of 1.4 to 1.0 and smelted in an electric furnace where the electric tips are in contact with molten slag prevent ing local overheating by open arcs.	Production of phosphoric acid and potassium phosphate.
1,492,713	1924	Do.....	Phosphate rock, silica carbon, electric furnace.	Materials are smelted in an electric furnace where the electric tips are in contact with molten slag prevent ing local overheating by open arcs.	Production of phosphoric acid.
1,513,088	1924	Charlton, H. W.....	Phosphate rock, sand, coke, air blast, and electric furnace.	Phosphate rock, sand and coke are fused in an electric furnace and the molten slag poured through a blast of air.	Production of phosphoric acid and slag wool.
1,514,512	1924	Kneib, B. G.....	Phosphate rock, sand or silicate, coke, ammonia, electric furnace, Cottrell precipitator.	Phosphate rock, silica and coke are smelted in an electric furnace. The phosphorus in the evolved gases is collected in a Cottrell precipitator.	Production of ammonium phosphate and carbon monoxide gas.
1,518,019	1924	Tulman, R. D.....	Phosphate rock, sand, coke, ferro-phosphorus, electric or blast furnace.	70 parts phosphate rock, 35 parts sand, 90 parts coke and 20 parts ferro-phosphorus are smelted in a suitable furnace. The ferro-phosphorus acts catalytically to volatilize the phosphorus.	Production of phosphorus or phosphoric acid.

TABLE LXXI.—PROCESSES AND APPARATUS DIRECTLY OR INDIRECTLY RELATED TO THE VOLATILIZATION OF PHOSPHORUS AND PHOSPHORIC ACID.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
282,118	1883	Reese, J.	Iron, phosphoric silicious slag, carbonaceous vapor.	Molten iron is subjected to fusion with phosphoric silicious slag in presence of carbonaceous gases.	Production of ferrophosphorus.
588,267	1897	De Chalmot, G.	Electric furnace.	An electric furnace with overflow outlet which allows fused material to fall on rolls covered continuously with sand.	Electric furnace for fusing phosphate rock.
724,142	1903	Stevenson, Jr., J.	Manganiferous iron ore, phosphoric flux.	Manganiferous iron ore is smelted with a phosphoric flux.	Production of phosphoric ferro manganese.
1,044,957	1912	Washburn, F. S.	Phosphate, silica, and carbon.	This invention relates to an electric furnace.	Production of phosphoric acid.
1,089,784	1914	Peacock, S.	P ₂ O ₅ vapors, hot water.	Spray P ₂ O ₅ vapors with water at 90° C. to 100° C.	Hydration of P ₂ O ₅ .
1,115,471	1914	Miller, D. I.	Phosphorus bearing material, iron bearing material, coke, heat.	Materials are charged into a blast furnace.	Production of ferro-phosphorus.
1,129,513	1915	Peacock, S.	Special electric furnace, nitrogen, material desired to be compounded with nitrogen.	Materials mixed with finely divided carbon are fed down between two electrodes while nitrogen is forced up. The finished product is withdrawn as fast as formed.	Production of compounds containing nitrogen.
1,142,371	1915	Schmitz, F. C.	Phosphate material, silica, carbon, heat, special absorption towers.	Phosphate material, flux, and reducing agent are fused and volatilized gases are oxidized and absorbed in special towers. The gases pass through body of liquid to remove solid matter.	Production of phosphoric acid.
1,142,397	1915	Burroughs, J. W.	Phosphate material, flux, heat, special absorption apparatus.	Fuse materials and decompose the phosphoric gas evolved by water, without cooling the gas below a predetermined temperature, in a special absorption apparatus.	Production of phosphoric acid.
1,149,233	1915	Washburn, F. S.	Phosphate rock, silica, carbon, heat, H ₂ SO ₄ .	Phosphate rock, silica and carbon are heated in an electric furnace. The silico phosphates of the volatilized gases are broken up by sulphuric acid and subsequently removed, leaving a pure phosphoric acid.	Production of high-grade phosphoric acid.
1,168,495	1916	Gray, Jr., J. J.	Natural phosphate, silica, carbon, metals, blast furnace.	Materials are fluxed and P ₂ O ₅ driven out of slag.	Production of phosphorus and metallic phosphide.
1,173,960	1916	Hechenbleikner, L.	Electric furnace, phosphate rock, silica, carbon.	Special type of water-cooled electric furnace for smelting phosphate rock, silica and carbon.	An electric furnace for producing phosphoric acid.
1,202,837	1916	Do.	Electric furnace for production of phosphoric acid.	The blast furnace is charged with a mixture of nelsonite ore, carbon, silica and phosphate material.	Electric furnace for producing phosphoric acid.
1,216,306	1917	Gray, Jr., J. J.	Nelsonite containing phosphate and iron oxide, carbon, fluxing material, blast furnace, phosphatic material.	Special water-cooled electric furnace. Cooled walls lined with chilled slag.	Production of ferrophosphorus from nelsonite.
1,217,306	1917	Hechenbleikner, L.	Electric furnace for phosphate treatment.	Materials are smelted in a blast furnace maintaining a predetermined temperature at top and in fusion zone.	Water-cooled electric furnace.
1,220,416	1917	Gray, Jr., J. J.	Iron ore, fluxing material, phosphate rock, carbon, blast furnace.	Special water-cooled electric furnace for treating phosphate rock.	Production of ferrophosphorus.
1,226,264	1917	Schmitz, F. C.	Electric furnace.		Water-cooled electric furnace.

TABLE LXXI.—PROCESSES AND APPARATUS DIRECTLY OR INDIRECTLY RELATED TO THE VOLATILIZATION OF PHOSPHORUS AND PHOSPHORIC ACID—Continued.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
1,241,971	1917	Wagman, W. H., Bryan, H., and Wagner, C. R.....	Blast furnace for producing phosphoric acid.	A blast furnace provided with an inner charge chamber surrounded by an outer chamber in which the evolved gases burn.	Phosphate smelting blast furnace.
1,242,987	1917	Schmitz, F. C.....	Phosphate rock, silica, carbon, heat, oxygen, special oxidation chamber for gases.	Phosphate rock, silica and carbon are heated and the volatilized gases are passed through a tortuous path in which oxygen is introduced in direction opposite to flow of gases. The P_2O_5 gas is then absorbed in towers.	Process of oxidizing phosphorus gases.
1,249,392	1917	Hechenbleikner, I....	Phosphorus and other gases, oxygen, special oxidation chamber.	The gases to be oxidized are subjected to a number of fine oxygen sprays countercurrent to flow of gases, so as to give a swirling motion.	Process of oxidizing phosphorus and other gases.
1,264,236	1918	Webster, H. A.....	Iron phosphate, carbon, siliceous flux, heat.	Materials are heated in a closed furnace until substantially all the oxygen of the phosphate has combined with carbon.	Production of ferrophosphorus.
1,264,237	1918	Do.....	Iron phosphatic material, carbon siliceous flux, rotary furnace, heat.	Materials are charged into a rotary furnace maintaining a reducing temperature and incandescent carbon.	Production of ferrophosphorus.
1,264,510	1918	Hechenbleikner, I....	Volatilized P_2O_5 and SiF_4 gases, electric precipitator, absorption towers.	The volatilized gases are first passed through an electric precipitation where the P_2O_5 gases are recovered. The remaining SiF_4 gas is absorbed in water in towers operating on counter-current principle.	Process of condensing phosphoric acid and hydrofluosilicic acid.
1,264,511	1918	Do.....	Volatilization gases P_2O_5 and SiF_4 , cooling chamber, electric precipitator, special absorption system.	The volatilized gases are passed through water-cooled chamber to an electric precipitator where the P_2O_5 is removed. The SiF_4 is then recovered in a special system of absorption and condensing tanks.	Process of cooling and condensing gases, such as P_2O_5 and SiF_4 , to produce phosphoric acid and hydrofluosilicic acids.
1,265,149	1918	Webster, H. A.....	Phosphate rock, silica, carbon, rotary furnace, heat.	Mixture of phosphate rock, silica, and carbon, is heated to above 1000° C. in a rotary furnace, and the slag and ferrophosphorus collected.	Production of ferrophosphorus.
1,268,849	1918	Jeffs, L. A.....	Phosphate rock, carbon, electric furnace, metals (copper, etc.).	Phosphate rock, carbon, and metal are fused in an electric furnace.	Production of P_2O_5 and phosphorus metallic alloys.
1,282,994	1918	Wagman, W. H., Wagner, C. R., and Bryan, H.	Mineral phosphate, silica, carbonaceous matter, fuel furnace, heat.	Mix phosphate mineral with silica and carbonaceous matter. Feed this mixture down a shaft into reaction zone where volatile constituents are driven off, surrounding the central shaft, thus preheating fresh charge. Phosphorus compounds are recovered from volatile products.	Process for manufacturing phosphorus and phosphoric compounds.
1,283,398	1918	Carothers, J. N., and Ross, W. H.....	Phosphorus oxide fumes, electric precipitator.	Phosphorus oxide fumes are precipitated at a temperature above 100° C. and provided with necessary moisture to give a crystalline phosphoric acid on cooling.	Production of a crystallized phosphoric acid.

TABLE LXXI.—PROCESSES AND APPARATUS DIRECTLY OR INDIRECTLY RELATED TO THE VOLATILIZATION OF PHOSPHORUS AND PHOSPHORIC ACID—Continued.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
1,284,200	1918	Merz, A. R., W. H., and Carothers, J. N.	Phosphorus fumes, substances to react with phosphoric oxide (steam, ammonia, KCl, etc.).	Volatilized phosphorus fumes are treated with a substance which will react with phosphoric fumes. The resulting compound is collected on a filter. The resulting phosphoric acid is precipitated from conc. H_3PO_4 by adding either CaCl_2 or sodium phosphate.	Recovery of volatilized phosphorus fumes.
1,299,336	1919	Hechenbleikner, I.	Combination electric furnace and mixing chamber.	Materials are charged to the mixing chamber through a rotary kiln. Coke is charged to mixing chamber directly. Materials are then pushed into electric furnace by mechanical stokers operating in mixing chamber.	Furnace for treating phosphate and other ores.
1,325,145	1919	Davis, J. D.	Phosphine, oxygen, carbonaceous catalyst, ammonia.	Selective oxidation of phosphine in presence of oxygen, ammonia and other gases is accomplished by passing through chamber containing catalytically active carbon. Hydrophobic acid is precipitated from conc. H_3PO_4 by adding either CaCl_2 or sodium phosphate.	Apparatus and process for oxidizing phosphine.
1,329,273	1920	Ross, W. H.	Concentrated H_3PO_4 , CaCl_2 , sodium phosphate.	Natural phosphates, siliceous materials and carbon are ignited in kiln to produce a porous material which is fed into electric furnace with carbon where phosphorus is evolved. The turning phosphorus preheats fresh charge and is then collected.	Process of removing hydrofluoric acid from concentrated phosphoric acid.
1,373,471	1921	Washburn, F. S.	Natural phosphate, siliceous material, carbon, electric furnace.	A combination blast and open hearth furnace in which the phosphate charge is fed through shaft onto hearth where flames and hot blast keep material in a molten condition until P_2O_5 is evolved.	Process of sintering phosphate charge for electric furnace treatment.
1,387,817	1921	Wagman, W. H., and Furey, T. B.	Combination blast and open hearth furnace, fuel, blast.	Materials are melted in a blast furnace and part of the gases withdrawn from lower part of shaft. Phosphorus is condensed in a special chamber and the remaining gases filtered through coke.	Fuel furnace for producing phosphorus and phosphoric acid.
1,441,573	1923	Franchot, R., and McElroy, K. P.	Phosphate rock, silica or silicates, coke, blast furnace.	Phosphorus in the gases from an electric furnace, smelting phosphatic material, is selectively oxidized by the introduction of limited quantities of air into the upper part of furnace or flues.	Production of phosphorus and carbon monoxide gas.
1,463,959	1923	Klugh, B. G.	A mixture of phosphorus vapor and carbon monoxide, air, or oxygen.	Ground phosphatic mineral P_2O_5 values produced by volatilization. The phosphoric acid is constantly activated.	Production of phosphoric acid and carbon monoxide gas.
1,470,968	1923	Gooch, S. D.	Phosphate mineral, mist of phosphoric acid.	The exit gases from furnace are used to preheat air for burning furnace through wet and dry stages. The hot air enters furnace through wet stage and then through dry stage level and between the electrodes in order to oxidize the evolved phosphorus within the furnace.	Production of fertilizer (monocalcium phosphate).
1,496,230	1924	Klugh, B. G.	Electric furnace, heat recuperative apparatus.	Hot air for burning phosphorus gases within furnace is obtained by first passing hot gases through regenerative checker brick to preheater, then passing the air in the reverse direction to the furnace.	Apparatus for smelting phosphatic materials.
1,497,173	1924	Hechenbleikner, I.	Phosphate rock, sand, coke, electric furnace, air.	Hot air for burning phosphorus gases within furnace is obtained by first passing hot gases through regenerative checker brick to preheater, then passing the air in the reverse direction to the furnace.	Method of oxidizing phosphorus and CO gases.
1,497,727	1924	Klugh, B. G.	Electric furnace, heat recuperative chambers, electrical precipitator.	Hot air for burning phosphorus gases within furnace is obtained by first passing hot gases through regenerative checker brick to preheater, then passing the air in the reverse direction to the furnace.	Apparatus for the production of phosphoric acid.
1,534,828	1925	Barr, J. A.	Phosphate rock, water, phosphoric acid, briquetting machine, dryer.	5 parts of 50% phosphoric acid and 8 parts of water are mixed with 100 parts of phosphate rock, and briquetted.	Briquetting of phosphate rock.

TABLE LXXII.—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES CONTAINING TWO OR MORE FERTILIZER INGREDIENTS.

U S Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
16,111	1856	Dickell, Charles	Feldspar, phosphate of lime, lime.	Ingredients are heated together and treated with water.	Products are a double silicate of aluminum and lime, phosphate of lime, lime, all insoluble in water; and caustic potash and a little caustic lime soluble in water.
26,196	1859	Mapes, J. J.	Bones (100), H_2SO_4 (56), guano (36), $(NH_4)_2SO_4$ (20).	Ingredients are thoroughly mixed.	Production of phosphatic nitrogenous fertilizer.
35,417	1862	Harper, Louis	Nitrogenous organic matter, H_2SO_4 , guano.	Allowed to stand.	Restoration of guano.
39,519	1863	Wilson, Geo. F.	Bone sulphate residue remaining after treatment of bones with H_2SO_4 ; ammonia (obtained by distillation).	Ingredients are thoroughly mixed.	Production of "binitro phosphate."
49,891	1865	Klett, F.	Feldspar, carbonate or hydrate of lime, fluoride of calcium, phosphate of lime or iron.	Constituents are mixed and calcined at a red heat for about 5 hours.	Products are a soluble silicate of lime and aluminum and a phosphate of potassium or sodium.
61,870	1867	Reimer, F.	Soil (16), KNO_3 (1), $(NH_4)_2SO_4$ (21), ground bone (1).	Constituents are mixed and cured.	Production of an economic fertilizer.
72,026	1867	Grimes, W. C.	Ground bone (8 bushels), Na_2SO_4 (80 pounds), H_2SO_4 (180 gallons), lime (40 gallons), soil (10 bushels).	Ground bone, Na_2SO_4 , and H_2SO_4 are mixed. Urine and soil are added after two hours.	Production of an improved fertilizer.
77,840	1868	Ramsburgh, J. S.	Bone (100), $(NH_4)_2SO_4$ (25), boiling water (3 gallons), H_2SO_4 (25 gallons), Na_2SO_4 (60 pounds), $CaSO_4$ (125 pounds), slaked lime (150 pounds), ashes.	Bones, $(NH_4)_2SO_4$, boiling water, and H_2SO_4 are mixed. While the mixture is hot Na_2SO_4 , $CaSO_4$, slaked lime, and ashes are added.	Improvement in fertilizer.
78,730	1868	Fales, Levi S.	Raw bones, leather, blood, H_2SO_4 , sludge, NH_3 gas, peat or sea sand.	Materials are thoroughly mixed.	Improvement in manufacture of fertilizer.
88,443	1869	Burkholder and Wilson	Bone dust, oil of vitriol, Na_2SO_4 , Na_2O_2 , $NaCl$, plaster, potash, sand.	Do.	Improvement in fertilizers.
90,037	1869	Cart, David	Phosphate rock, potash solution, lime, gypsum.	Alternate layers of phosphate moistened with caustic potash solution and lime are compacted. Gypsum may be added on barreling the material.	Production of "the persicator."
100,437	1870	Stupard, C. U., Jr.	Quicklime, ammoniacal water of gas works, H_2SO_4 , phosphatic material.	Quicklime is mixed with the ammoniacal water and the mixture is heated. The liberated ammonia is absorbed by H_2SO_4 , but not to saturation, leaving the product in a fluid state. This fluid is then poured over phosphatic material.	Production of an ammoniated superphosphate.

TABLE LXXII.—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES CONTAINING TWO OR MORE FERTILIZER INGREDIENTS.—Continued.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
100,729	1870	Commis, J.	Gas liquor, blood, H_2SO_4 , steam, phosphate rock.	Mixture is evaporated to dryness.	Improvement in fertilizers.
110,084	1870	Spence, Peter	Aluminum phosphate, H_2SO_4 , NH_3 , sawdust.	Phosphate is ground and mixed with H_2SO_4 . Mixture is heated until solution is completed. NH_3 gas is run into the solution. After alum has been allowed to crystallize out, the solution is run upon sufficient sawdust to absorb it.	Production of material for the manufacture of alum and an artificial fertilizer.
124,964	1872	Manwaring and Birch	Cottonseed hulls, lime, H_2O .	Hulls are burned and the ashes taken up with water. Lime is added and the solution decanted.	KOH and $Ca_3(PO_4)_2$
135,995	1873	McDougall, J.	Acid phosphate, sawdust, NH_3 .	Ammonia vapors are absorbed by acid phosphate mixed with sawdust.	Improvement in fertilizers.
206,077	1878	Boykin and Carmer ..	Dissolved bone, plaster, $NaNO_3$, Na_2SO_4 , $(NH_4)_2SO_4$, ashes, peat.	Materials are thoroughly mixed.	Improved fertilizer.
246,121	1881	Graf, Leopold	Liquid leather (obtained by boiling tanned scrap leather with KOH and water under pressure), gypsum, phosphate rock, H_2SO_4 .	Materials are mixed and heated to drive off moisture.	Do.
317,010	1885	Pierce, W. S.	Aluminum and iron phosphate, $(NH_4)_2SO_4$, oil of vitriol.	Phosphate and $(NH_4)_2SO_4$ are pulverized, mixed, treated with acid, and dried.	Phosphate nitrogen fertilizer.
345,625	1886	Dunne, J. J.	Phosphates, K_2SO_4 , Na_2SO_4 , coal.	Mixture is roasted to a temperature just below fusion.	Phosphate of potash.
353,210	1886	Dudley, D. W.	Bone meal (1), wood ashes (1), H_2O , lime, acid, gypsum, and $NaCl$.	Lime is slaked in brine, mixed with gypsum and sodium chloride, and the whole mixed with bone meal and wood ashes.	Improved fertilizer.
374,201	1887	Petracus, Carl V.	Phosphate of lime, H_2SO_4 , water, K_2SO_4 , K_2CO_3 or KOH .	Phosphate is ground and treated with H_2SO_4 . Mass is leached with water and K_2SO_4 is added to the solution. The solution is then filtered and K_2CO_3 added. On heating this solution the lime, magnesium, aluminum, and iron phosphates separate out. The remaining solution is filtered, evaporated, and cooled.	Acid phosphate of potash.
395,532	1889	Williams, Wm. J.	Oil of vitriol, nitrogenous matter, water, phosphate rock.	Nitrogenous matter is acidulated, phosphate rock moistened, and the two mixed.	Improved fertilizer.
396,274	1889	Endemann, H.	Tobacco stems, oil of vitriol, phosphate rock.	Tobacco stems are treated with oil of vitriol and the acid neutralized with phosphate rock.	Do.
404,348	1889	Do.	Do.	Tobacco is treated with phosphate rock.	Do.
446,815	1891	Glaser, C.	Crude phosphoric acid, alkali salt.	The leachings being used to treat some basic material, fused mass dissolved in water and boiled. Treat with alkali carbonate until alkaline. Separate by crystallization or otherwise.	Process of making alkaline phosphates.
450,253	1891	Reese, Jacob	Basic slag, ammonium salt.	Materials are ground and mixed thoroughly.	Calcareous phosphate ammonium fertilizer.

TABLE LXXII.—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES CONTAINING TWO OR MORE FERTILIZER INGREDIENTS—Continued.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
450,254	1891	Reese, Jacob	Phosphatic slag, potassium salts.	Materials are ground and mixed.	Production of available K_2O and P_2O_5 .
450,255	1891	Do.	Basic slag, ammonium salt, K_2O .	Do.	Phosphatic nitrogenous potash fertilizer.
450,531	1891	Do.	Basic slag, KCl .	Materials are ground and mixed thoroughly.	Phosphate potash fertilizer.
484,631	1892	Dunne, J. J.	Phosphate rock, nitrogenous organic matter, oil of vitriol.	Materials are mixed and dried.	Improved nitrogen fertilizer.
535,076	1895	Pieper, A. R. O.	Aluminum phosphate, potash, lye, lime.	Materials are thoroughly mixed.	Production of citrate-soluble P_2O_5 .
601,089	1898	Wiborgh, J. G.	Apatite, carbonate of sodium or potassium or caustic soda or potash, heat.	Mixture is heated.	Production of citrate-soluble tetracalcium sodium (or potassium) phosphate.
620,443	1899	Goldsmith, W. L.	Phosphate rock, soft coal, H_2SO_4 , K_2 and nitrogenous matter.	Materials are mixed thoroughly.	Improved fertilizer.
709,185	1902	Terne, Bruno	Phosphate rock, oil of vitriol, NH_3 liquor.	Do.	Do.
731,461	1903	Jarecki, A. K.	Phosphate rock, oil of vitriol, waste bettsugar alcohol slop, addition of absorbents or driers.	Do.	Fertilizer.
897,695	1908	Young, J. R.	Phosphate rock, H_2SO_4 , organic ammoniates.	Do.	Production of ammoniated acid phosphate.
911,282	1909	Do.	Organic ammoniates, phosphate rock, sulphuric acid, potash.	Materials are mixed.	Production of complete fertilizer.
936,317	1909	Halvorsen, B. F.	Phosphate rock, HNO_3 , $Ca(NO_3)_2$.	Phosphate rock is dissolved in HNO_3 and the excess of moisture taken up with calcined $Ca(NO_3)_2$.	Production of solid fertilizer containing P_2O_5 and N .
988,894	1911	Peacock, Samuel	Commercial calcium cyanamid, phosphoric acid.	Cyanamid is intimately and rapidly mixed with phosphoric acid; temperature not to rise above $150^\circ C$.	Mixture of calcium phosphate and calcium cyanamid.
1,001,350	1911	Caro and Scheele	F_2PO_3 , H_2SO_4 , NH_3 .	NH_3 gas passed into H_2PO_3 .	Stable nonhygroscopic ammoniated superphosphate.
1,018,186	1912	Haff, M. M.	Feldspar, calcium phosphate, heat.	Feldspar and phosphate are heated together in a furnace. Phosphoric acid and potash are volatilized together.	Production of potassium phosphate and a slag which may be used for glass making.
1,020,293	1912	Kieghiel, Carl	Solution of acid sodium phosphate, KCl , NH_3 , HCl .	KCl is introduced in the solution of acid sodium phosphate, and the solution is boiled. Potassium phosphate is procured by repeated boiling and crystallization. For the manufacture of $NH_4H_2PO_4$, the acid sodium phosphate solution is neutralized with NH_3 gas. The precipitate is filtered off and HCl added to the filtrate.	Production of potassium or ammonium phosphate.

TABLE LXXII.—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES CONTAINING TWO OR MORE FERTILIZER INGREDIENTS—Continued

U. S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
1,016,909	1912	Sagblich, Ludwig	Material phosphates containing carbonates, nitric acid, and moisture	Phosphate is evolved to nitric acid in presence of nitric	Production of available phosphoric acid and calcium nitrate or nitrate or both
1,040,081	1912	Wilson, T. L. and Hafl, M. M.	Material phosphates containing moisture	Ammonia is introduced into the liquid and partly mass of calcium phosphate	Production of dry nitrogenous phosphate fertilizer
1,046,322	1912	Peterson, Benjamin	Phosphate rock, fish manure, etc.	Minerals are treated with phosphoric acid and water, then with water under pressure	Production of phosphate fertilizer
1,050,006	1912	Peterson, Benjamin	Phosphate rock, water, etc.	Phosphate rock is treated with water under pressure	Production of material containing calcium phosphate and dicalcium phosphate
1,050,037	1912	Collett, Emil	Phosphate of lime, nitric acid, etc.	Phosphate of lime is treated with nitric acid and water	Production of material containing calcium phosphate and dicalcium phosphate
1,050,145	1912	Baun, T. W.	Phosphate rock, which contains iron and calcium carbonate	Phosphate rock is treated with nitric acid and water	Production of a fertilizer containing monocalcium phosphate and calcium nitrate
1,058,249	1913	Meriwether, C. N.	Phosphate rock, lime, etc.	Phosphate rock is treated with lime and water	Production of a fertilizer
1,062,869	1913	Wilson, T. L. and Hafl, M. M.	Superphosphate, nitric acid, etc.	Nitric acid is added to superphosphate and water	Nitrogen containing phosphate
1,069,151	1914	Nicholas, F. C.	Calcium phosphate, nitric acid, etc.	Calcium phosphate is treated with nitric acid	Production of available P_2O_5 and K_2O
1,100,618	1914	Whishburn, F. S.	Phosphate rock, nitric acid, etc.	Phosphate rock is treated with nitric acid	Production of soluble NH_3 and P_2O_5
1,103,115	1914	Do	Calcium phosphate, nitric acid, etc.	Calcium phosphate is treated with nitric acid	Production of a nitrogenous and phosphate fertilizer
1,103,910	1914	Wilson, T. L. and Hafl, M. M.	Phosphate rock, nitric acid, etc.	Phosphate rock is treated with nitric acid	Production of a nitrogenous and phosphate fertilizer
1,111,490	1914	Perrino, J. C.	Potash containing silicate, phosphate, etc.	Potash containing silicate, phosphate, etc. is treated with water	Production of a fertilizer
1,112,183	1914	Wilson, T. L. and Hafl, M. M.	Double superphosphate, NH_3 , etc.	Double superphosphate is treated with NH_3 gas	A dry nitrogenous phosphate fertilizer

TABLE LXXII—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES CONTAINING TWO OR MORE FERTILIZER INGREDIENTS—Continued

U. S. Pat. No.	Date	Patente	Reagents Used	Treatment	Object of Process
1,115,044	1914	Washburn, F. S.	Crude phosphoric acid, NH_3 (gas, house liquor), steam	Mix hot gas house liquor with hot crude phosphoric acid and bubble steam through recovering light ppt of ammonium phosphate	Production of ammonium phosphate
1,122,183	1914	Wilson, T. L., and Haft, M. M.	Superphosphate, NH_3 gas	Damp pasty superphosphate is treated with dry NH_3 gas	Production of a nitrogenous phosphate fertilizer.
1,127,840	1915	Do.	Acid phosphate, NH_3 gas	Acid phosphate is dried to contain 6 or 7% moisture and NH_3 gas added	Production of an ammoniated acid phosphate
1,129,514	1915	Peacock, S.	Phosphate rock, carbon, nitrogen, heat	Mixture of phosphate rock and carbon in atmosphere of nitrogen, to volatilize phosphorus and carbonitriles	Process for producing phosphorus and fixing nitrogen
1,129,722	1915	Do.	Natural phosphates, nitrogen, carbon, heat	Heat mixture of phosphate and carbon in atmosphere of oxygen or in an atmosphere of nitrogen collecting evolved gases and burning to produce oxides, or treating with steam under pressure to produce NH_3 and $(\text{NH}_4)_2\text{PO}_4$	Production of available P_2O_5 and nitrogen.
1,142,068	1915	Washburn F. S.	Phosphoric acid, NH_3	Add NH_3 to phosphoric acid sol until slightly alkaline and then add acid until acid to chemical indicator.	Production of mono ammonium phosphate
1,144,405	1915	Willson T. L. and Haft, M. M.	Alkali mineral SO_3 alkaline earth phosphate, heat.	Materials are fused and the fused mass treated with suitable reagent to dissolve the alkali phosphate, or fused mass finely ground	Production of a fertilizer containing an alkali
1,145,107	1915	Do.	Phosphoric acid, phosphate rock, potash, NH_3 gas	Add phosphoric acid and potash to phosphate rock, and then neutralize the excess acid with NH_3 gas	Improved fertilizer composition containing K_2O , P_2O_5 and NH_3
1,146,222	1915	Do.	Pyrophosphoric acid, phosphate rock, NH_3 gas	Phosphate rock is treated with pyrophosphoric acid to produce a double superphosphate. NH_3 gas is then introduced to combine with free acid and monocalcium phosphate	Production of double superphosphate containing some ammonia
1,149,390	1915	Merwether, C. N.	Phosphate material, iron, lime and magnesia salts, K_2O , Na_2O , heat	Mix phosphate material, iron lime and magnesia salts, additive in turn. To molten mass add potash and soda oxide. Grind and use with or without extruding the material	Production of a basic phosphate fertilizer.
1,150,899	1915	Srinckler E. H.	Alkali metal phosphate, phosphorus free acid	An alkali metal phosphate is treated with a phosphorus free acid (H_2SO_4 , HCl etc.), and the solution concentrated to separate out the alkali salt of added acid.	Production of a mono alkali phosphate.
1,159,900	1915	Do.	Phosphate material, acid sodium sulphate, carbon heat (H $_2$ SO $_4$, HCl etc.)	Heat phosphate material and sodium sulphate and carbon thus produce a solution of free H_2PO_4 and NH_3 gas. Free hum phosphate is then treated with the H_2PO_4 to produce monosodium phosphate	Production of mono alkali phosphate.

TABLE LXXII—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES CONTAINING TWO OR MORE FERTILIZER INGREDIENTS—Continued

U. S. Pat. No.	Date	Patente	Reagents Used	Treatment	Object of Process
1,151,074	1915	Washburn, F. S.	Phosphate rock, H_2SO_4 , NH_3 , and special ammoniating apparatus	Phosphate rock treated with H_2SO_4 in special tank to produce HPO_4 , which is filtered and ammoniated in special towers	Apparatus for making ammonium phosphate
1,151,633	1915	Do	Mon ammonium phosphate, heat, vacuum	Heat in no ammonium phosphate solution to about 112° C. until moisture is reduced to predetermined amount and then subjected to vacuum to further remove moisture	Production of dry granular mono ammonium phosphate
1,163,130	1915	Connor, T. H.	Blatt furnace slag, phosphoric acid, soda ash, lime, field spar, heat	Materials are ground mixed and calcined to render phosphate and potash partly water soluble	Production of a fertilizer
1,166,104	1915	Willcox, T. L. and Hall, I. S.	Mono calcium ammonium phosphate fertilizer material	Mono calcium ammonium phosphate and ammonium phosphate are mixed with a fertilizer material	Improved fertilizer
1,167,738	1916	Washburn, F. S.	Crude phosphoric acid, NH_3 gas, steam	One portion of crude acid is treated with an excess of test and NH_3 gas and another portion treated with a deficiency of NH_3 . The two portions are then mixed	Production of mono ammonium phosphate
1,168,55	1916	Herzka, E.	Molasses refuse, phosphate material, H_2SO_4	Molasses residue is concentrated mixed with ground phosphate and the mixture treated with H_2SO_4	Production of a potash, nitrogen and phosphate fertilizer
1,172,420	1916	Bassett, H. P.	Phosphate rock, felspathic rock, alkali metal acid sulphate car	The felspathic rock is heated with alkali metal acid sulphate rendering potash water soluble. Phosphate rock is treated with the acid fumes evolved and P_2O_5 made available. A special type of furnace is used	Production of soluble potash and phosphate
1,194,077	1916	Ross, W. H. Merz, A. R. and Carothers, J. N.	NH_3 gas, water vapor, oxidized phosphorus gases	Volatilized phosphorus oxide vapor is treated with NH_3 gas in presence of water vapor	Production of dry concentrated fertilizer containing available P_2O_5 and nitrogen
1,196,910	1916	Washburn, F. S.	Calcium cyanamid, $(NH_4)_2SO_4$, acid phosphate	Mix calcium cyanamid and $(NH_4)_2SO_4$ together and add enough acid phosphate to take up the liberated NH_3	Production of a fertilizer containing calcium cyanamid, $(NH_4)_2SO_4$, and acid phosphate
1,208,877	1916	Wollenweber, W.	Phosphoric acid, NH_3 gas	NH_3 gas is passed into solution of phosphoric acid until solution is slightly alkaline and maintaining the reaction temperature at 110° C	Production of acid ammonium phosphate
1,212,196	1917	Thomas, G. H. Earp	Phosphate rock, cell grass humus, potassium and nitrogen	Mix ground phosphate rock and cell grass with other fertilizer constituents	Fertilizer composition
1,214,346	1917	Messerschmitt, A.	Potash bearing mineral phosphate limestone, nitrate, heat	Phosphate material, a potash bearing mineral and lime stone are calcined and then treated with 25% $Ca(NO_3)_2$ in hot solution, and dried	Production of non hygroscopic fertilizer
1,251,742	1918	Blumenberg, Jr., H.	$(NH_4)_2SO_4$, phosphate rock	Heat phosphate rock and ammonium sulphate together in the presence of water	Process of making ammonium phosphate

TABLE LXXII.—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES CONTAINING TWO OR MORE FERTILIZER INGREDIENTS—Continued.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
1,258,106	1918	Gardiner, R. F.	Apatite, $(\text{NH}_4)_2\text{SO}_4$, heat.	Finely ground apatite and ammonium sulphate are fused together at about 500°C .	Production of a phosphatic, nitrogenous fertilizer.
1,264,513	1918	Hechenbleikner, I.	Phosphoric acid, NH_3 gas.	NH_3 gas is introduced into a bath of dilute phosphoric acid (about 40% P_2O_5) utilizing the heat of neutralization to evaporate water from bath producing dry ammonium phosphates.	Production of mono and diammonium phosphates.
1,264,514	1918	Do.	Phosphoric acid, NH_3 gas, heat.	A stream of phosphoric acid is subjected to a stream of NH_3 gas flowing in opposite directions. The heat of neutralization plus an external source of heat is utilized to dry the crystals of amm. phosphate formed.	Production of mono and diammonium phosphate.
1,272,001	1918	Borgiesani, G., and Stampa, G.	Phosphatic mineral, potassic mineral, sodium bisulphate, heat.	The materials are heated to fusion and powdered.	Production of citrate soluble phosphoric acid and potash.
1,275,276	1918	Lie, E.	Cyanamid, superphosphate, water, acid anhydrid.	A mixture of cyanamid and superphosphate is treated with water and an acid anhydrid and allowed to react.	Production of a fertilizer containing available P_2O_5 and nitrogen.
1,276,555	1918	Meadows, T. C.	Hydrous potassium mineral (Glauconite) acid phosphate.	A hydrous potassium mineral (such as glauconite) is ground and mixed with water to form a sludge, which is treated with commercial acid phosphate to form a potassium phosphate.	Production of mono and diammonium phosphate.
1,276,555	1918	Cameron, F. K.	NH_3 gas, phosphoric acid, pressure.	Strong solution of phosphoric acid is treated with NH_3 gas under pressure to precipitate out $(\text{NH}_4)_2\text{PO}_4$.	Process of treating phosphoric acid solution.
1,280,650	1918	Bosch, C.	Urea, superphosphate, NH_3 gas.	Urea and superphosphate are ground together and dried by air or NH_3 gas.	Fertilizer containing calcium urea phosphate and NH_3 .
1,282,385	1918	Delacourt, A. F.	Tri calcium phosphate material, potassium containing silicate.	Materials are heated to about 1100°C .	Production of available phosphoric acid and potash.
1,282,805	1918	Gardiner, R. F.	CaCl_2 , P_2O_5 , potassium bearing mineral, wood waste, heat.	The mixed materials are heated to a bright red.	Production of a fertilizer containing available P_2O_5 and potash.
1,285,122	1918	Glaeser, W.	Potassium bearing silicate, sodium phosphate, heat.	Potassium bearing silicates are heated, then suddenly cooled, ground and mixed with finely ground sodium phosphate, and heated to above 1000°C .	Method of treating potassium bearing silicates to render potash soluble.
1,285,203	1919	Fuss, A.	Phosphate containing some calcium carbonate, HNO_3 .	Phosphate material containing some calcium carbonate is treated with nitric acid, and while in the semi-liquid state, a current of air is passed through the mass.	Production of a phosphate fertilizer containing nitrogen.
1,299,337	1919	Hechenbleikner, I.	Phosphate rock, feldspar, carbonaceous matter, electric furnace, rotary kiln.	Phosphate rock and feldspar are charged through a rotary kiln preheated by volatilized gases. Coke is charged direct. Materials are then heated to volatilize potash and phosphate. The gases are oxidized and condensed. Impurities SiO_2 and SiF_4 in gases are removed by chemical action of incoming charge.	Production of phosphate and potash fertilizer.

TABLE LXII—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES CONTAINING TWO OR MORE FERTILIZER INGREDIENTS—Continued

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
1,310,080	1919	Henwood, A	Phosphate rock, acid sulfate, potash, ash, aluminum silicate, niter cake	finely ground phosphate rock or potash silicate mixed with acid sulfate or niter cake is subjected to a fine stream of water sufficient to hydrate the calcium sulfate formed	Production of phosphate and potash fertilizer
1,350,591	1920	Carothers, J N	calcium phosphate, HNO_3 , calcium cyanamid containing free lime	calcium phosphate is treated with HNO_3 to produce a mixture of calcium nitrate and calcium nitrite which is treated in succession with cyanamid containing free lime	Product and process of making soluble calcium phosphate, calcium nitrate, and cyanamid
1,354,719	1920	Bolire, A C	insoluble phosphate, urea, formalin, cyanuric acid, HNO_3	insoluble phosphate is treated with a urea salt or solution of cyanuric acid and nitric acid	Production of fertilizer containing soluble phosphate and nitrogen
1,355,369	1920	Wachburn, I S	calcium cyanamid phosphate, NH_3 gas	free nitrogen crystals are extracted with hot water and the extract is treated with phosphoric acid and filtered to give a solution is then acidified with NH_3 and concentrated	Production of nitrogenous phosphate material
1,357,120	1920	Sadtler, S S	calcium monohydrogen phosphate, alkali metal or ammonium salt of acid capable to form insoluble salt with calcium cyanamid concentrated phosphoric acid	calcium monohydrogen phosphate is treated with an alkali or ammonium salt of an acid capable of forming an insoluble calcium salt	Process of making an alkali or ammonium acid phosphate
1,360,401	1920	Heffernan, P C	calcium cyanamid, free lime, dilute phosphoric acid	calcium cyanamid containing free lime is treated with concentrated phosphoric acid in proportions to form a calcium monohydrogen phosphate	Production of fertilizer containing monohydrogen phosphate
1,366,560	1921	Kilmer, A L	phosphate material, potassium bearing silicate, alkali metal salt, bent	phosphate material is treated with dilute phosphoric acid in proportions to produce calcium phosphate and a silicate which is separated by filtering	Production of fertilizer materials, calcium phosphate and ammonium phosphate
1,367,940	1921	Washburn, I S	phosphate rock, mineral acid, NH_3	soluble phosphate and potash fertilizer are mixed and calcined to produce a mixture which is treated with sufficient mineral acid to give a solution which is filtered with sufficient mineral acid to give a solution of phosphate in acid. The mixed acid is then neutralized with NH_3	Process and production of a soluble phosphate and potash fertilizer
1,369,763	1921	Hetherington, H C and Brahm, F M	phosphate, NH_3 gas	concentrated phosphoric acid is treated with NH_3 until the slushy acid. The heat of neutralization being sufficient to concentrate solution to a point where crystals of ammonium phosphate separate out	Process and production of crystalline mono ammonium phosphate
1,377,553*	1921	Bloom, I E	phosphate of lime, potassium base, nitrogen gas, special etc., treating apparatus	positively charged calcium phosphate is compounded with negatively charged nitrogen or potassium base and nitrogen in special electrifying apparatus	Production of a compound fertilizer

* Note — Abstract of claims Nos 22 and 33

TABLE LXXII.—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES CONTAINING TWO OR MORE FERTILIZER INGREDIENTS—Continued.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
Patent No.	1921	Bloom, J. E.	Molten phosphatic slag, phosphate material, NH_3 gas, potash material, electricity.	Phosphate material is electrically compounded with slags, NH_3 , N_2 or potash materials.	Production of a compound fertilizer by utilizing furnace slags.
1,411,696	1922	Haage, T.	Natural phosphates, potassium bearing silicates, marl, heat.	Materials are broken up, mixed, and melted. Remove, mull and disintegrate by high pressure fluid, collecting and grinding the fine particles.	Production of a potash and phosphate fertilizer.
1,413,013	1922	Edgar, Graham	Calcium cyanamid, phosphate rock, mineral acid.	Calcium cyanamid is treated with a mineral acid in excess of that required for decomposing lime (free and combined). The excess acid is neutralized with phosphate rock.	Process and production of fertilizer containing urea and available P_2O_5 .
1,413,168	1922	Kreiss, A. L.	Phosphate rock, alkali salt, rotary drier.	Phosphate rock heated highly and plunged into solution of potassium or sodium salt explodes allowing an intimate mixture to be formed, which is further calcined in reducing temperature in rotary drier.	Production of a fertilizer containing potash or sodium and available phosphate.
1,413,048	1922	Matheson, A.	Alunite, phosphate rock, water, heat.	Alunite is heated to 901.8°C . in a mechanically rabbled muffle furnace. The SO_3 and SO_2 gas evolved is absorbed by moistened phosphate rock forming acid phosphate. The calcined alunite is mixed with phosphate rock.	Production of acid phosphate, and a phosphate potash fertilizer.
1,417,248	1922	Huson, J.	Ammonium sulphate (336 lbs.), acid phosphate (448 lbs.), potassium chloride (90 lbs.), manganese sulphate (45 lbs.), wood ash (45 lbs.) and soil (1275 lbs.).	Materials are mixed, exposed to air eight days, wet and dried. To be used in cellar for planting potatoes.	Fertilizer containing nitrogen, potash and phosphate.
1,420,596	1922	Webster, H. A.	Manure or organic matter (containing nitrogen), acid phosphate, and phosphatic limestone.	The materials are ground and thoroughly mixed. The organic ammonia is fixed by the acid phosphate.	Production of fertilizer containing nitrogen and phosphoric acid (P_2O_5).
1,434,055	1922	Clarkson, F., and Braden, J. M.	Urea, phosphoric acid (55 to 75% H_3PO_4).	Urea is added to 75% phosphoric acid in molecular proportions, cooled and urea phosphate crystallized out.	Production of urea-phosphate.

* † Note:—Abstract of claims Nov. 16, 18, 19, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 60, and 61.

TABLE LXXVI.—PROCESSES FOR THE PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES CONTAINING TWO OR MORE FERTILIZER INGREDIENTS—Continued.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
1,441,694	1923	McElroy, K. P.	Potash silicates, iron, flux, carbon, blast furnace, phosphoric acid.	Potash silicate, iron, flux and carbon are fused in a blast furnace. The fumes evolved are collected and treated with phosphoric acid to produce a high-grade fertilizer.	Production of ammonium and potassium phosphate.
1,456,830	1923	Hazen, W., and Ross, W. H.	Phosphoric acid (70 to 90%), potassium chloride, ammonia gas.	Potassium chloride (1 molecular wt.) is treated with phosphoric acid (2 molecular wts.) heated to drive off hydrochloric acid and the excess phosphoric acid neutralized with ammonia gas.	Production of fertilizer containing K_2O , P_2O_5 and NH_3 .
1,456,851	1923	Ross, W. H., and Hazen, W.	Potassium chloride (2 gm. mols.), phosphoric acid (70 to 90%) (3 gm. mols.), heat.	Potassium chloride is treated with phosphoric acid heated to 250° C. and air bubbled through it. The hydrochloric acid is driven off and the potassium phosphate remaining is separated from the excess phosphoric acid by crystallization.	Production of potassium phosphate.
1,469,507	1923	Glaeser, W.	Potassium silicate, calcium chloride, coke, iron oxide, phosphate rock, steam heat 1200° F.	The materials are heated in a muffle furnace to 1200° F. and steam passed through, liberating lime and hydrochloric acid. The lime combines with the phosphate rock to form tetraphosphate. Potassium chloride is leached out.	Production of available phosphate and the extraction of potassium compounds.
1,495,270	1924	Sillesen, J. N. A.	Phosphate rock, calcium cyanamid, carbon dioxide and water, heat.	Phosphate rock and calcium cyanamid are treated with carbon dioxide and water.	Production of available P_2O_5 and a mixture containing calcium cyanamid.
1,510,179	1924	Liljenroth, F. G.	Phosphorus, nitrogen, pressure, heat.	Phosphorus and nitrogen are heated to about 900° C. at a pressure of 1000 atmospheres.	Production of phosphorus nitride.
1,542,986	1925	Breslau, J., and Darner, G.	Calcium cyanamid, carbon dioxide, phosphate rock, potassium salt.	Calcium cyanamid is treated with CO_2 and water to obtain a solution of free cyanamide, which is converted by potassium bisulphate into urea. Excess acid is neutralized with phosphate rock.	Production of a fertilizer containing urea and available P_2O_5 .

TABLE LXXIII.—PROCESSES FOR THE PRODUCTION OF SOLUBLE PHOSPHATE BY ELECTROLYSIS.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
669,271	1901	Denbergh, F. P. Van	Apatite, etc., siliceous flux, electric current, oxygen, steam or water vapor.	Apatite is crushed and together with the flux is placed in an electric furnace. Phosphorus is liberated by electrolysis in an atmosphere containing an excess of oxygen. The resultant P_2O_5 is hydrated by leading steam into the furnace.	Method of producing pure phosphoric acid.
690,048	1901	Cheeseman, Lewis ..	Phosphate rock, $NaHSO_4$, H_2SO_4 , HNO_3 or HNO_3 electricity.	Phosphate rock is intimately mixed with $NaHSO_4$ solution, and a current of electricity is passed through the mixture.	Production of mono-calcium and di-calcium phosphates.
707,886	1902	Whorugh, J. G., and Palmaer, W.	Apatite or other mineral phosphate, a salt of such composition that during electrolysis an acid which forms a soluble salt with lime and a basic hydrate are formed, water, electricity.	Salt solution is the electrolyte. Phosphate is placed in the solution near the anode. Calcium phosphate is precipitated at cathode end, collected, and dried.	Production of citrate-soluble phosphate.
748,523	1903	Palmaer, Wilhelm ..	Salt solution as above, mineral phosphate, CO_2 .	During electrolysis the acid and alkaline solutions are drawn off separately. The acid solution is made to act on phosphate in a separate vessel. The alkaline solution is added until the acid reaction disappears, bicalcic phosphate being precipitated. The filtrate is mixed with the rest of the cathode solution and CO_2 led in. This precipitates the lime and regenerates the electrolyte.	Method of producing bicalcic phosphate.
819,410	1906	Clemm, Adolf	Mineral phosphate or bones, etc., HCl, electricity.	Phosphate is treated with HCl. The solution is separated from the residue and neutralized. It is then electrolyzed, chlorine being evolved at the anode and hydrogen at the cathode. At the cathode a precipitate of $Ca_3H_2P_2O_8$ is formed.	Production of chlorine and citrate-soluble phosphate.

TABLE LXXIV.—PROCESSES FOR THE ENRICHMENT OF PHOSPHATES.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process
86,574	1869	Otologin, A. M.	Water or air, phosphate rock.	Phosphate is ground under water and heavier particles separated by difference of specific gravity.	Method of concentrating phosphate rock.
789,647	1905	Arens, Richard	Water, superphosphate, heat, calcium bisulphate solution containing phosphate (formed by treating phosphate with sulphurous acid).	Superphosphate is leached with water, giving a solution of monobasic calcium phosphate. This solution is heated and the calcium bisulphate solution run into it. Sulphurous acid is given off and collected.	Production of dibasic calcium phosphate free from sulphurous acid.
971,830	1910	Coates, L. R.	Mineral which is composed of phosphate and carbonate of lime and phosphatic fossil, heat, air.	Mineral is burned and slaked by exposure to air. The material is then screened, and the coarser particles (largely lime phosphate) are ground and added in predetermined proportion to the material that has passed the screen.	Process of unification and enrichment.
1,014,254	1912	Pratt, N. P.	Earthy deposits consisting of phosphate or lime and calcium sulphate saline solution such as sea water	Earthy material is treated with sea water, which dissolves the calcium sulphate, leaving behind the phosphatic material in a loose condition.	Process of enrichment.
1,014,255	1912	Do.	Acid phosphate or other phosphate containing sulphate, suitably selected, such as water	Phosphate is treated with a solvent which dissolves the sulphate, leaving the phosphate behind.	Do.
1,129,407	1915	Lay, W. F.	Natural phosphate rock, H_2SO_4 or other acid, washing machine for removing alkaline impurities	Solution in saturating dilute dissolving carbonates and other impurities. The rock is then washed with water and dried.	Process of removing impurities in phosphate rock.
1,161,473	1915	Haff, M. M. and Willson, T. L.	Phosphate material, NH_3 gas, pressure	The phosphate material is dried by passing air and NH_3 gas into a closed vessel under pressure.	Process of drying and enriching a phosphate material.
1,192,545	1916	Memminger, C. G.	Natural phosphates, heat	Natural phosphate containing SiO_2 and CaO is heated to decompose the $CaCO_3$. CO_2 is driven off and the CaO combines with SiO_2 .	Method of enriching phosphate material.
1,266,730	1918	Webster, H. A.	Phosphatic limestone, heat.	Phosphatic limestone is heated until the $CaCO_3$ is converted to CaO . The lighter CaO particles are separated from the heavier phosphate particles by air currents.	Process of concentrating a low-grade phosphatic limestone.
1,453,571	1923	Stevenson, E. P.	Phosphate rock, heat.	Poible phosphate containing moisture and calcium carbonate is calcined at 1800 to $2000^\circ F$ driving off moisture and CO_2 , forming a more basic lime phosphate.	Process of increasing the P_2O_5 content in phosphate rock.
1,535,120	1925	Kanowitz, S. B., and Webster, H. A.	Phosphate rock, drier, pulverizer and air separator.	Phosphate rock is dried, pulverized and the coarse particles separated from the fine by air separation. The coarse particles having a higher P_2O_5 content.	Process for separating high-grade phosphate rock from lower grades.
1,547,732	1925	Broadbridge, W., and Edser, E.	Phosphate rock, water, sodium silicate, oleic acid, and flotation equipment.	Phosphate rock ground to 80 mesh is agitated with 4 times its weight of water to which 1 lbs. of sodium silicate (per ton of rock) is added. While being agitated and aerated 2 1/2 lbs. of oleic acid is added drop by drop. The froth on the surface floats off the higher grade rock.	Process of separating high-grade phosphate rock from its impurities.

TABLE LXXV.—PROCESSES AND APPARATUS FOR THE MECHANICAL TREATMENT OF PHOSPHATE ROCK AND SOLUBLE PHOSPHATES.

U.S. Pat. No.	Date	Patente	Reagents Used	Treatment	Object of Process or Apparatus
75,328	1868	Wilson, G. F.	Grinding and disintegrating apparatus.	Machine with self-adjusting granite rollers for mixing and grinding acid phosphate with farinaceous matter.	Improvement in acid phosphate manufacture.
75,330	1868	Do.	Steam or hot air, acid phosphate.	Acid phosphate is exposed in thin sheets and steam or hot air passed over it.	Production of dry acid phosphate.
75,331	1868	Do.	Acid phosphate, screening.	Acid phosphate is put through screens.	Separation of coarse from fine material.
75,332	1868	Do.	Bones, furnace for burning same.	Bones are placed in a special form of furnace and burned to whiteness.	Production of colorless bone ash.
75,333	1868	Do.	Acid phosphate, mill for disintegrating.	The acid phosphate is disintegrated in a special form of mill in such a way as not to heat the acid phosphate.	Production of pulverulent acid phosphate.
75,334	1868	Do.	Acid phosphate, grinding and screening.	The acid phosphate is granulated in a special mill and passed through screens.	Production of finely pulverized acid phosphate.
75,335	1868	Do.	Acid phosphate, lead and gutta-percha pump.	The acid phosphate is conveyed by a pump made of lead and gutta-percha.	Form of non-corrosive pump for acid-phosphate liquor.
75,337	1868	Wilson, G. F., and Horsford, E. M. .	Acid phosphate, farinaceous material, drying platforms, heat.	The acid phosphate is mixed with farinaceous material and spread on drying platforms having a temperature of 75° F.	Production of dry acid phosphate.
86,289	1869	Duvall, A.	Phosphate rock, H ₂ SO ₄ , steam blast.	The phosphatic material and H ₂ SO ₄ are mixed by blowing a blast of steam against the materials as they issue from a spout.	Apparatus for mixing H ₂ SO ₄ with pulverized phosphate rock.
102,648	1870	Baugh, E. T.	Guano or acid phosphate, spread on series of gratings, through which hot air is passed.	Guano or acid phosphate is spread in layers over a series of gratings, through which hot air is passed.	Production of dry phosphatic fertilizer.
105,319	1870	Duvall, A.	Acid phosphate and cylindrical bin.	After mixing the acid and phosphate rock the product is discharged into a special form of bin.	Production of a better acid phosphate.
106,147	1870	Frank and Adt	Acid phosphate, special form of dryer.	Acid phosphate is put through a special form of cylindrical dryer.	Production of dry acid phosphate.
114,693	1871	Lewis, Geo. T.	Phosphate rock, water, grinding mill.	The phosphate rock is ground in a mill with water.	Improvement in method of grinding phosphate.
335,673	1886	Bacon, E. C.	Phosphate rock, washing machine.	The phosphate rock is washed in a special form of machine.	Improvement in method of washing phosphate rock.
371,083	1887	Lord, V.	Phosphate rock, grinding and bolting apparatus.	Phosphate rock is ground and passed through bolting mill along with balls of hard material which help grind the rock and prevent bolting cloth from clogging.	Apparatus for preparing phosphate rock for fertilizers.
627,276	1899	Huttmann, J.	Apparatus for making phosphoric acid.	Phosphate rock and H ₂ SO ₄ are fed into two agitators in series and then to centrifugal machine where acid is separated. It is then run into several concentrators and a cooler.	Apparatus for making phosphoric acid.
1,036,896	1912	Peacock, S.	Hygroscopic materials, C ₂ H ₅ (PO ₃) ₂ H ₂ O; K ₂ H ₂ (PO ₃) ₂ H ₂ O; etc.; NH ₃ gas.	Hygroscopic materials caused by excess acidity are rendered non-hygroscopic by subjecting them to an atmosphere of NH ₃ gas.	Process of rendering commercial salts non-corrosive.
1,093,141	1914	Lynen, G. H.	Superphosphate.	Phosphate is decomposed in bin with movable platform which engages with movable side walls.	Apparatus for use in manufacture of superphosphate.

TABLE LXXV.—PROCESSES AND APPARATUS FOR THE MECHANICAL TREATMENT OF PHOSPHATE ROCK AND SOLUBLE PHOSPHATES.—Continued.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process or Apparatus
1,124,442	1915	Hoover, F. K., and Mason, A. J.	Natural phosphate rock, triturating machine.	Clay and iron impurities are loosened from phosphate rock preliminarily to screening by machine containing a set of stationary and a set of revolving arms.	Triturating device to prepare phosphate rock for screening and washing.
1,129,407	1915	Lay, W. F.	Natural phosphate rock, H_2SO_4 , or other acid, washing machine for removing alkaline impurities.	Screened phosphate rock is subjected to a weak acid solution in rotating drum, dissolving carbonate and other impurities. The rock is then washed with water and dried.	Process of removing impurities in phosphate rock.
1,137,551	1915	Praet, G. L.	Phosphate, H_2SO_4 , special acid phosphate machinery.	Phosphate dust mixed with acid delivered to special system of curing dens.	Production of acid phosphate.
1,151,074	1915	Washburn, F. S.	Phosphate rock, H_2SO_4 , NH_3 and special ammoniating apparatus.	Phosphate rock treated with H_2SO_4 in special tank to produce HPO_3 , which is filtered and ammoniated in special towers.	Apparatus for making ammonium phosphate.
1,151,833	1915	Do.	Mono ammonium phosphate, heat, vacuum.	Process of heating mono ammonium phosphate solution to about $112^{\circ}C$ until moisture is reduced to predetermined amount, and then subjected to vacuum to further remove moisture.	Production of dry granular mono-ammonium phosphate.
1,161,473	1915	Haff, M. M., and Willson, T. L.	Phosphate material, NH_3 gas, pressure.	The phosphate material is dried by passing air and NH_3 gas into a closed vessel under pressure.	Process of drying and enriching a phosphate material.
1,325,145	1919	Davis, J. D.	Phosphine, oxygen, carbonaceous catalyst, ammonia.	Selective oxidation of phosphine in presence of oxygen, ammonia and other gases is accomplished by passing through chamber containing catalytically active carbon.	Apparatus and process for oxidizing phosphine.
1,376,612	1921	Forbis, R. E.	Den, mixing and elevating machinery, phosphate, H_2SO_4 .	Amalgam den, with rotating top platform, on which is placed a mixing machine, and an excavating machine for removing cured material. The process is continuous.	Acid phosphate apparatus.
1,383,911	1921	Doyle, W. T.	Phosphate rock, H_2SO_4 , special den and mixing apparatus.	Phosphate rock is mixed with H_2SO_4 and delivered to special den with means for discharging from den, and with means for adding an additional amount of phosphate rock, and means for pulverizing mixture.	Apparatus for manufacturing acid and superphosphates.
1,383,912	1921	Do.	Phosphate rock, H_2SO_4 , acid phosphate apparatus.	Ground phosphate rock is mixed with H_2SO_4 and delivered to den where reaction takes place. Pulverize and add phosphate dust to take up excess acid.	Process for making acid and superphosphate.
1,393,840	1921	Shield, M.	Special rotary kahn, and nozzle for projecting slurry means of removing reaction vapors.	Phosphate rock slurry is projected into reaction zone of mutually fired rotary kahn through special nozzles.	Apparatus for calcining phosphate rock.
1,398,816	1921	Tuttle, A. L.	Superphosphate den, means of removing reaction vapors.	Vapors are removed from den by being allowed to escape from joints below the charge level.	Method of removing reaction vapors from acid and superphosphate dens.
1,401,527	1921	Doyle, W. T.	Phosphate rock, H_2SO_4 , special acid phosphate apparatus.	Phosphate rock and H_2SO_4 are continuously mixed and charged into moving den. The movement of den is so regulated that reaction is complete when it reaches the disintegrators.	Apparatus for making acid phosphate and superphosphate.

TABLE LXXV.—PROCESSES AND APPARATUS FOR THE MECHANICAL TREATMENT OF PHOSPHATE ROCK AND SOLUBLE PHOSPHATES—Continued.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Process and Apparatus
1,403,820	1922	Sturtevant, T. J.	Acid phosphate apparatus.	Phosphate rock and H_2SO_4 are mixed and discharged into an inclined den with disintegrating apparatus at lower end. An endless conveyor prevents mass from getting stuck in den.	Apparatus for making acid phosphate or superphosphate.
1,403,820	1922	Do.....	Acid phosphate apparatus (inclined den with conveyor at the bottom and disintegrator at lower end).	A mixture of phosphate rock and sulphuric acid is fed into a den with an inclined floor. After the material has "set" a conveyor at bottom of den drags the block of acid phosphate into the blades of a disintegrator and aerator.	Apparatus for the manufacture of acid phosphate.
1,418,618	1922	Butt, C. A.	Nitrates or nitrites, free acid or acid salt iron filings.	Iron filings are mixed with acid phosphate containing nitrates or nitrites. The nascent hydrogen produced reduces the nitrate to ammonia which combines with any free acid.	Conditioning of fertilizers.
1,428,920	1922	Sturtevant, T. J.	Acid phosphate apparatus (rotary carrier with pockets to receive acid-rock mixture).	Phosphate rock and sulphuric acid are mixed and discharged into pockets on a revolving carrier. These pockets discharge (on lower part of orbit) into a disintegrator and aerator.	Apparatus for making acid phosphate.
1,428,921	1922	Do.....	Acid phosphate apparatus (vertical rectangular den with feed screw down the center), disintegrator at lower end.	A mixture of phosphate rock and sulphuric acid is fed into the upper part of den and after "setting up" is carried downward by a screw to the disintegrator.	Apparatus for making acid phosphate continuously.
1,428,522	1922	Do.....	Acid phosphate apparatus (den with hinged sides and excavator on movable carriage).	A mixture of phosphate rock and sulphuric acid is fed into the den, and after "setting," the sides are loosened and the carriage with excavator moves forward slicing off the acid phosphate with cutter blades. Aeration is accomplished by the fan-like effect of the cutter blades.	Apparatus for the manufacture of acid phosphate.
1,430,621	1922	Bruhn, G. A.	Apparatus, a box conveyor the sides of which form a continuous channel, a mixer and a disintegrator.	A mixture of acid and phosphate rock is introduced at one end and is set and aged by the time it reaches the cutter disintegrator at the other end of conveyor.	Continuous process and apparatus for making superphosphate.
1,439,054	1922	Armstrong, E. H. ...	Acid phosphate, cutter, and aerating towers, hot air.	Fresh acid phosphate is fed through a cutter, onto a cone which distributes it on a revolving disk which throws the material to the sides where it falls into the next cone and the operation is repeated while hot air passes counter current. A second tower aerates with cool air.	Process and apparatus for conditioning acid phosphate.
1,499,611	1924	Gravell, J. H.	Phosphoric acid, phosphorus pentoxide, and water free solvent as butyl alcohol.	100 parts of 85% phosphoric acid is treated with 30.4 parts of phosphorus pentoxide and the product dissolved in an equal volume of butyl alcohol.	Method of preparing anhydrous phosphoric acid.

TABLE LXXXVI — PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES BY MISCELLANEOUS PROCESSES

U S Pat. No	Date	Patentee	Reagents Used	Treatment	Object of Patent
54,635 67,315	1866 1867	Wister, J H Moore, J H	Bones of pig Oyster or clam shells, H_2SO_4	The ingredients are thoroughly mixed and ground in a mill and mixed with H_2SO_4 as in the manufacture of acid phosphate	The gypsum facilitates grinding soluble fertilizer
156,181	1874	Siebel J E	Phosphoric acid bones NH liquor	The phosphoric acid after being used in treating bones is recombined with the crude NH_3 liquor. The NH_3 is distilled off and the acid again	Process of recovering phosphoric acid and purifying ammonia
171,857	1876	Ravenel St J	Phosphate rock iron pyrites	The ingredients are ground and thoroughly mixed and the mixture is then treated with water	The gradual formation of soluble phosphates
209,980 238,133	1878 1881	Pirz A Lewis Geo T	Phosphate rock $CaSO_4$ broken pyrites	The phosphate rock is mixed with water and the mixture is then exposed to weathering	Production of available P_2O_5
241,868	1881	Irvine G A	Phosphate rock carbon heat	The phosphate rock is treated with carbon and heated to high temperature	Do
421,320	1890	Hudkins L R	Phosphate rock CaO water	The phosphate rock is mixed with water and heated to high temperature	Do
453,749	1891	Van Rynbake T	Aluminum phosphate stick CaO	The stick is treated with CaO and heated to high temperature	Production of dry product containing available P_2O_5
493,859	1892	Chateau I	Hydrated phosphates of iron and aluminum	Mixture is treated to high temperature and allowed to cool	Production of available P_2O_5
507,444	1893	Recht H	Aluminum phosphate and sulfuric acid	The mixture is treated to high temperature and allowed to cool	Process of obtaining meta and orthophosphoric acid combinations
517,661	1894	Powder N B	Aluminum phosphate and sulfuric acid	The mixture is treated to high temperature and allowed to cool	Production of fertilizer
517,662	1894	Do	Do	Do	Do
714,330	1902	Reese Jacob	Phosphate rock oxides of iron and manganese	The mixture is treated to high temperature and allowed to cool	Process of making fertilizer described in Patent No. 517,662
789,440	1905	Michalske F J	Phosphate rock Na_2CO_3 heat	The mixture is treated to high temperature and allowed to cool	Production of citric soluble phosphate
792,314	1905	Chisolm Wm B	Phosphate rock sulphur CaO water	The mixture is treated to high temperature and allowed to cool	Production of PCl_3 and $Na_2C_2N_2$
824,280	1906	Do	Phosphate rock sulphur nitrogen bearing materials	The mixture is treated to high temperature and allowed to cool	Production of available P_2O_5
824,281	1906	Do	Phosphate rock sulphur nitrogen	The mixture is treated to high temperature and allowed to cool	Production of fertilizer containing available P_2O_5
947,795	1910	Coates L R	Sterilized culture mixture containing microorganisms and food for bacteria, phosphate rock	The mixture is treated to high temperature and allowed to cool	Process of preparing mixture for fertilizer described in Patent No. 824,280
947,796	1910	Do	Do	Do	Production of available P_2O_5 and K ₂ O from insoluble minerals

TABLE LXXVI.—PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES BY MISCELLANEOUS PROCESSES—Continued.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Patent
1,002,143	1911	Frerichs, F. W.	Phosphate rock (NH_4SO_4), heat, water.	Phosphate rock and $(\text{NH}_4)_2\text{SO}_4$ are mixed and roasted till a temperature of 500°C . is attained. NH_3 and H_2O escape and a mixture of calcium metaphosphate and CaSO_4 remains in retort. This is treated with water. The humus or peat is first sterilized by heat or borax wa-te. It is then mixed with phosphate rock; lime and material containing nitrifying bacteria are added. Saccharine material may be added to aid growth of bacteria.	Production of calcium metaphosphate and ammonia.
1,002,248	1911	Ellis, Carleton	Phosphate rock or basic slag, humus or peat, borax waste, lime, saccharine material, nitrogen-assimilating bacteria cultures, heat.		Production of available P_2O_5 and process of producing same.
1,024,880	1912	Coates, L. R.	Phosphate rock high in carbonate, heat, sulphuric acid.	Phosphate rock is heated until the carbonate present is all converted into CaO . This is slaked and treated with small amount of sulphuric acid.	Available phosphoric acid free of acidity.
1,032,763	1912	Newberry, S. B., and Barrett, H. N.	Phosphate rock, carbon, heat, air.	Phosphate rock and carbon are ground and mixed. The mixture is then strongly heated, first in reducing atmosphere and then in oxidizing flames. Product is ground.	Production of citrate-soluble P_2O_5 .
1,104,326	1914	Stoltzenberg, H.	"Vinasse" (spent wash from sugar beets, or wine), phosphoric acid, acid phosphate, or superphosphate, heat.	Materials are mixed and evaporated to dryness.	Production of a non-hygroscopic fertilizer.
1,129,504	1915	Peacock, S.	Phosphate material, carbon, nitrogen, heat.		
1,147,926	1915	Chisolm, W. B.	Sulfur, phosphate rock, steam.	Phosphate material intimately mixed with carbon is heated from 900° to 1300°C . in atmosphere of nitrogen or an atmosphere devoid of oxygen to produce phosphorus carbide, or Carbonitride of Phosphorus.	Process of separating phosphorus from phosphate combinations.
1,222,112	1917	Lipman, J. G.	Phosphate rock, sulfur, fertile soil, rotted manure.	Finely ground sulfur and phosphate rock are moistened and packed tightly to initiate the formation of sulfuric acid.	Production of fertilizer.
1,235,906	1917	Do.	Sulfur, phosphate material, bacteria capable of oxidizing sulfur.	Vulx materials and keep moist so that sulfur be oxidized by bacterial action to acid which will render phosphate citrate soluble.	Production of citrate-soluble phosphates.
1,244,445	1918	Blumhurg, Jr., H.	Phosphate material, NH_3 , CO_2 .	Mn , saltpetre (1), bacteria material (1), phosphate (2 to 10), sulfur finely ground and apply to soil. Bacteria oxidize sulfates and produce sulfuric acid which renders phosphates available.	Fertilizer composition.
1,261,025	1918	Hoff, J. N.	Phosphate rock, acid phosphate, humus bacteria.	Treat ground phosphate material with NH_3 and CO_2 in presence of water to form CaCO_3 and ammonium phosphate. The $(\text{NH}_4)_2\text{PO}_4$ is heated to drive off NH_3 and form phosphoric acid which is treated with phosphate material to produce an acid calcium phosphate.	Production of acid calcium phosphate.
1,316,196	1919	Snelling, W. O.	Fertilizer material, explosive.	Digest humus with phosphate with bacteria.	Process of making a fertilizer.
1,348,495	1920	James, C. C.	Acid phosphate, CaCO_3 , lime.	Polymerized fertilizer material held together by a cementing material is mixed with an explosive.	Process and production of an explosive fertilizer.
				Dry pulverulent acid phosphate, CaCO_3 and lime are mixed together.	Production of a di-calcium phosphate fertilizer containing CaSO_4 , lime and CaSO_4 .

TABLE LXXVI.—PRODUCTION OF SOLUBLE OR AVAILABLE PHOSPHATES BY MISCELLANEOUS PROCESSES—Continued.

U.S. Pat. No.	Date	Patentee	Reagents Used	Treatment	Object of Patent
1,348,990	1920	Giesecke, A.	Corn steep acid waste water, milk of lime.	Corn steep acid waste water is partially neutralized with milk of lime.	Production of a combination of protein and phosphate of calcium.
1,361,596	1920	Lipman, J. G.	Sulfur, sulfofying bacteria.	Dry sulfur and sulfofying bacteria are mixed to contain 0.5 to 5.0% of bacteria.	Sulfur composition containing sulfofying bacteria.
1,393,839	1921	Stoeld, M.	Phosphate rock, heat, rotary kiln.	Phosphate slurry is projected suddenly to a heat of about 1100 to 1400° C. in a rotary kiln.	Process of calcining phosphate rock and rendering phosphate rock soluble.
1,393,840	1921	Do.	Special rotary kiln, and nozzle for projecting slurry.	Phosphate rock slurry is projected into reaction zone of specially formed rotary kiln through special nozzles.	Apparatus for calcining phosphate rock.
1,425,747	1922	Chates, L. R.	Acid phosphate, lime water, heat, mill.	Lime chloride is added to acid phosphate to convert it to tricalcium phosphate. Wet, dry and ground.	Production of a non-acid fertilizer.
1,434,749	1922	Plauson, H.	Phosphate rock or basic slag, caustic, brown oval, disintegrating mill.	The phosphate, brown oval, and caustic liquor are ground together in a high speed disintegrating mill at 20 to 100° C.	Manufacture of a phosphatic manure.
1,445,187	1923	Do.	Phosphatic material, water and sulphuric acid.	Phosphatic material is ground with a large volume of water and a small amount of acid or alkali for several hours in a high speed mill.	Manufacture of a phosphatic manure.
1,451,786	1923	Ross, W. H., Durbin, C. B., and Jones, R. M.	Phosphoric acid (Sp. G. 1.85) cooling, crystallization.	Phosphoric acid is concentrated to a specific gravity of 1.85 at a temperature of less than 150° C., cooled, and crystallized. The crystal phosphoric is separated by centrifuging.	Purification of phosphoric acid by crystallization.
1,487,205	1924	Carothers, J. N., and Guthrie, A. B.	Phosphoric acid, and sodium silicate.	Fluorine compounds are removed from concentrated phosphoric acid by its dilution with sodium silicate and filtering through sand filters.	Purification of phosphoric acid.
1,493,009	1924	Bramson, C.	Lime water, sodium sulphate, phosphoric acid.	Crude phosphoric acid is treated with lime water, forming tricalcium phosphate, which is then treated with sodium sulphate.	Production of sodium phosphate from crude phosphoric acid.
1,493,100	1924	Do.	Lime water, sulphuric acid, phosphoric acid, calcination.	The residue from the purification of phosphoric acid by lime water is treated with excess lime water and the tricalcium phosphate formed is calcined, reentering the lime water.	Recovery of P ₂ O ₅ from residue obtained in the purification of phosphoric acid.
1,511,929	1924	Alcock, H. E.	Phosphoric acid, sodium phosphate, sodium carbonate, caustic soda, barium sulphide, sulphuric acid, filter.	Crude phosphoric acid is treated with sodium carbonate and caustic soda and this solution treated with barium sulphide. The barium phosphate is then treated with sulphuric acid to obtain a solution of pure phosphoric acid.	Preparation of pure phosphoric acid.
1,538,089	1925	Carothers, J. N., and Gerber, A. B.	Phosphoric acid, sodium sulphide, sulphuric acid, sodium silicate refrigerator, centrifuge.	Concentrated crude phosphoric acid is treated with sodium sulphide, sulphuric acid and sodium silicate and cooled to about 10° C. and inoculated with a seed acid.	Purification of phosphoric acid by crystallization.
1,538,910	1925	Stokes, W. E.	Mono calcium phosphate, calcium carbonate, and vacuum dryer.	A solution of mono calcium phosphate and free phosphoric acid is dried in vacuum dryer, and calcium carbonate added to take up the free acid.	Preparation of mono-calcium phosphate.
1,544,911	1925	Laist, F.	Phosphoric acid which contains vanadium, sodium or calcium ferrocyanide.	Vanadium is removed from phosphoric acid by precipitation with sodium or calcium ferrocyanide.	Purification of phosphoric acid.

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